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Long Range Transport of Airborne Pollutants (LRTAP) Aquatic Effects Monitoring

P. Brooksbank, J. Haemmerli, G. Howell and L. Johnston

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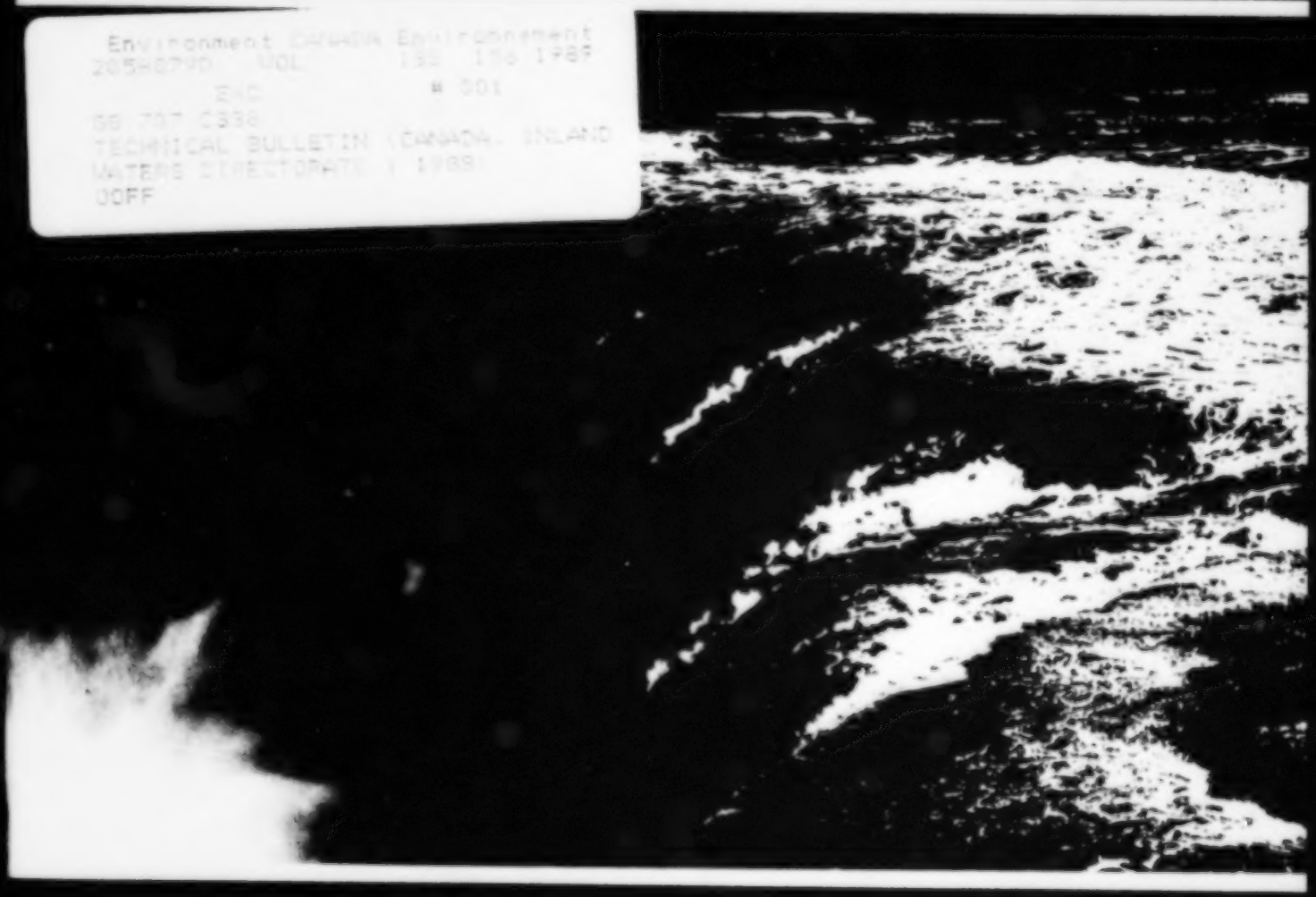

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Abstract

This report describes the rationale and design criteria used to develop the aquatic effects monitoring network of the Long Range Transport of Airborne Pollutants (LRTAP) Program. The selection of specific areas or locations where monitoring should be carried out was based on the atmospheric deposition and terrain sensitivity for those areas.

The appendices describe the implementation of the network in the Quebec and Atlantic regions and the recommended methods for the collection and analysis of water samples.

Résumé

Le présent rapport décrit l'objet et les critères de conception utilisés dans l'élaboration du Programme du réseau de surveillance des effets aquatiques du transport à distance des polluants atmosphériques (TDPA). Le choix des régions ou des emplacements particuliers où doit être effectuée la surveillance s'est fait en fonction des dépôts atmosphériques et de la vulnérabilité du terrain.

Les annexes décrivent la mise en application du réseau dans les régions du Québec et de l'Atlantique, et les méthodes recommandées pour le prélèvement et l'analyse des échantillons d'eau.

Foreword

This report describes the aquatic effects monitoring network of the Long Range Transport of Airborne Pollutants (LRTAP) Program, as well as the implementation of the network in the Atlantic and Quebec regions. The aim of this network is the integration of federal and provincial LRTAP aquatic monitoring activities into a comprehensive national water quality monitoring network, designed specifically to obtain the required water quality data and information to meet the needs of the departmental LRTAP program by effective and efficient use of the resources of contributing agencies. Such a network will provide a high quality compatible data base from which assessments of the status of Canada's lakes, rivers, and ground-water resources can be developed with respect to acid deposition.

It must be emphasized that LRTAP aquatic effects monitoring is a long-term project (i.e., more than 5 years). The hydrology, chemistry, and biology of surface water systems are highly variable both from year to year and within any given year. A trend in a water quality variable can only be established when several years of information indicate that a significant change in the level or response of the water quality variable has occurred. Some factors that can influence the variability of the water quality parameters of interest to the acid rain program are emission levels of acid rain precursors (SO_x, NO_x), transport and deposition levels (i.e., weather pattern changes from year to year, precipitation amounts and intensity), basin effects, productivity, natural cycles, land use changes, and changes in economic activity in the region. These factors can lead to highly variable data and cause year-to-year changes. Over the short term, erroneous conclusions can be drawn from this information.

The design and implementation described in this report will ensure that data collected by the different agencies involved are comparable. More detailed descriptions of the individual monitoring projects and protocols are included as appendices.

Long Range Transport of Airborne Pollutants (LRTAP) Aquatic Effects Monitoring

P. Brooksbank, J. Haemmerli, G. Howell and L. Johnston

1.0 INTRODUCTION

1.1 Need for Aquatic Effects Monitoring

In recent decades, the evidence indicates that an acid deposition problem parallel to that in northern Europe exists in North America. Extensive research has shown that sulphur and nitrogen oxide released to the atmosphere are transported hundreds and even thousands of kilometres, and are deposited as wet and dry deposition. In addition, much of eastern Canada is sensitive to acid deposition because of a lack of natural buffering capacity (Memorandum of Intent, 1983).

Historical data have shown that in Atlantic Canada the Atlantic salmon *(Salmo salar)* is endangered by acid rain. Nine salmon rivers in Nova Scotia have pH measurements below 4.7, and the fish have disappeared (Watt *et al.*, 1983). In Quebec and Ontario, thousands of lakes are reported to be acid stressed, and a smaller percentage are known to be severely limited in their ability to support aquatic life (Bobée *et al.*, 1982; Dillon, 1983; Kelso *et al.*, 1986). Acid rain is also considered as a threat in parts of western Canada; precipitation with a pH as low as 4.6 has been measured in the northern part of Saskatchewan, which forms part of the sensitive Canadian Shield. In southwestern British Columbia, probable transboundary air pollutants and emissions from metropolitan Vancouver provide a wet sulphate deposition rate in excess of 20 kg/ha per year.

Many lake and river surveys have been carried out across eastern Canada by federal and provincial agencies. These surveys have provided a data base from which the present status and extent of acidification of surface waters can be deduced. Research to determine the cause and effect relationship between acid deposition, terrestrial effects, and aquatic effects is in progress at five intensive study sites.

Except for the long-term data sets for the Atlantic coast rivers, however, there is a shortage of temporal data. Consequently, the rates of acidification and changes in the water quality over time cannot be assessed adequately for many aquatic ecosystems in eastern Canada.

In order to obtain the necessary data, an aquatic effects monitoring network designed to collect time-dependent water quality data is needed. This network will provide data that, when considered in the context of the existing survey data, will permit an assessment of the present quality of Canada's inland waters (surface and ground waters) and document the year-to-year changes with respect to acidification-related parameters.

The monitoring network will provide information for assessing the effectiveness of emission controls. The Canada/U.S. MOI negotiating team (Memorandum of Intent, 1983) requested that a LRTAP monitoring program be implemented to assess the effectiveness of any emission control agreement between Canada and the United States.

A comprehensive aquatic effects monitoring network is a key element in the provision of information to the LRTAP program management. Information from the monitoring network is essential for program managers to develop improved policies and to develop or refine the emission control programs.

1.2 Relationship of Aquatic Effects Monitoring to Other Components of the LRTAP Program

The linkages of LRTAP aquatic effects monitoring with aquatic effects research and modelling and other LRTAP monitoring programs are as follows.

Aquatic effects research in Canada has centred on the five intensive study sites located at the Experimental Lakes Area, Dorset, and Algoma in Ontario; Lac Laflamme in Quebec; and Kejimkujik National Park in Nova Scotia. Many aspects of the acidification processes and basin responses are being studied at these locations. This information is useful and necessary for the design of the aquatic effects monitoring network. In addition, models developed by the researchers will be helpful during the interpretation of the monitoring data. Conversely, because of the wealth of data and baseline information available, these study basins make excellent monitoring sites. It is anticipated that the monitoring network will continue to sample lakes in these areas even if the research program is reduced. In the meantime, data from the research studies will be used by the monitoring program.

The aquatic effects monitoring also has linkages with the atmospheric deposition monitoring (CAPMON) and emission inventories. Information from these projects should be mutually supportive and will allow an analysis of interrelationships between the atmospheric deposition and water chemistry changes.

2.0 OBJECTIVE AND GOAL

2.1 Objective

The objective of the LRTAP aquatic effects monitoring network is to define changes in time in the chemistry and biota of aquatic systems due to the long-range transport of airborne pollutants, focusing on acidic deposition. This objective provides a guide for the network design and defines the ultimate use of the data.

Monitoring is understood here to be the systematic collection of water or biological samples, usually at fixed locations, over an extended period of time (years), to be analyzed for a fixed suite of variables followed by the interpretation of the data in terms of the aquatic system reactions to the acidification stress.

The monitoring of short-term changes such as pH depression caused by a rapid snowmelt or a heavy rainstorm is presently beyond the scope of this network, although any lasting effects from these episodic changes should be detected by the long-term monitoring.

2.2 Goal

Given the objective above, it is then necessary to define a more specific goal, which would also serve as a guideline in the design of the network. The specific goal is to compare the chemical and biological responses of low alkalinity aquatic systems in different regions (geographic and geologic) receiving similar depositions of acidic materials and in regions having similar terrain sensitivity but subjected to differing deposition rates of acidic material. For ground waters, only highly sensitive waters in high loading areas will be monitored.

Low alkalinity aquatic systems, as defined here, are those having a calcium carbonate alkalinity of <500 µeq/L (<25 mg/L). This includes all waters having a low to extreme sensitivity to acid deposition, as defined by the Ontario Ministry of the Environment classification system (Table 1).

Table 1. Ontario Ministry of the Environment Lake Classification System for Surface Water Sensitivity to Acid Deposition*

Sensitivity	Alkalinity ($\mu eq.L^{-1}$ $CaCO_3$)
Acidified	≤0
Extreme	>0 to 39.9
Moderate	40 to 99.9
Low	100 to 499.9
Not sensitive	≥500

*Ontario Ministry of the Environment (1985).

3.0 MONITORING NETWORK DESIGN

3.1 Design Criteria

There are several kinds of change discussed in this report:

(a) Change in the value of a water quality variable over any given year for a particular water body (e.g., a lake).

(b) Change in the mean annual value of a water quality variable for a particular water body from year to year.

(c) Change in the mean seasonal value of a water quality variable for a particular water body from year to year.

(d) Any one of the above where change refers to a change in a mean for the entire region that will contain numerous water bodies.

An optimum sampling plan for measuring one type of change may not be optimal for another. The network focuses on detecting a change in the mean of the parameter for the entire region, i.e., local influences that may result in changes in individual lakes or streams will be averaged over the regional area where external stresses are common.

The magnitude of the change to be detected is also important. This will determine the number of samples to be collected from within the region of interest. One of the LRTAP program goals is to reduce emissions of sulphur dioxide by 50%. Therefore a monitoring network designed to detect a change of 10% in the concentrations of sulphate or alkalinity from year to year was agreed upon as a reasonable change to expect within one year.

The following was suggested as a guideline for the design of the aquatic effects monitoring network: "The monitoring will detect a yearly change in concentrations of sulphate and/or alkalinity or of major cations of 10%, with a confidence level of 90%, within a sensitive region."

At the present time sufficient data are not available to establish parameter variabilities and validate the appropriateness of the above guideline for all sensitive regions. Data are available, however, for Harp Lake, Ontario, and Lac Laflamme, Quebec. These lakes are located in research basins and are sampled on a weekly basis. The data in Table 2 show that the variability as measured by the standard deviation is 25% to 40% of the mean value for alkalinity and 10% to 30% for sulphate. Tables 3 and 4 show the data from Lac Laflamme by month and year. These data show that the variability within the fall season after turnover is much lower than the annual variability. By sampling after the fall overturn each year, comparing this data from year to year, and disregarding the variability within the year, the sampling is optimized and the water chemistry monitoring goals can be attained more efficiently.

Table 2. Mean Annual Concentrations of Sulphate and Alkalinity for Lac Laflamme, Quebec, and Harp Lake, Ontario

	Alkalinity (mg/L)		Sulphate (mg/L)	
	Mean	Std. dev.	Mean	Std. dev.
Lac Laflamme				
1981	5.085	2.256	4.644	1.417
1982	5.308	1.173	3.735	0.446
1983	5.422	1.280	4.052	0.350
Overall	5.336	1.390	4.144	0.954
Harp Lake 7 years of data (1976-1983)	5.359	2.213	9.799	3.130

Note: Samples collected weekly.

The efficiency of the monitoring network can be increased further by determining the change in the mean over the entire region in place of the change in the mean for a particular lake. The following procedure is used (M. Alvo, 1984, University of Ottawa, pers. com.).

Suppose there are N lakes in a particular region that have been stratified on the basis of geophysical and other characteristics such as basin area. Let there be strata and suppose that the h stratum contains N_h lakes.

Table 3. Mean Monthly Sulphate Values (mg SO_4^{2-}/L) for Lac Laflamme

	1981			1982			1983		
Month	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.
January	4	4.375	0.395	4	3.475	0.457	4	4.350	0.100
February	4	4.050	0.580	4	3.450	0.129	4	4.300	0.082
March	5	7.400	1.742	5	3.480	0.227	5	4.180	0.249
April	4	4.975	0.299	4	3.650	0.370	4	4.225	0.499
May	4	6.050	0.173	4	3.500	0.271	5	3.600	0.200
June	5	6.020	0.110	5	3.840	0.378	4	3.825	0.330
July	4	4.500	1.158	4	4.150	0.342	4	4.325	0.275
August	5	3.860	0.089	5	3.600	0.200	5	4.020	0.277
September	4	3.525	0.150	4	3.375	0.050	4	4.050	0.173
October	4	3.400	0.231	4	3.450	0.058	4	3.950	0.238
November	4	3.525	0.310	5	4.200	0.200	5	3.760	0.230
December	5	3.500	0.316	4	4.600	0.377	4	4.200	0.516

Table 4. Mean Monthly Alkalinity Values ($CaCO_3$ mg/L) for Lac Laflamme

	1981			1982			1983		
Month	N	Mean	Std. dev.	N	Mean	Std. dev.	N	Mean	Std. dev.
January	4	6.275	0.189	4	8.325	0.419	4	5.950	0.645
February	4	5.100	3.030	4	9.025	0.457	4	6.750	0.351
March	5	4.120	2.402	5	9.180	0.766	5	7.340	0.760
April	3	5.733	1.537	8	8.275	1.022	4	6.500	0.990
May	4	3.875	1.034	4	4.875	1.053	5	4.120	0.622
June	5	2.280	0.835	5	4.500	0.406	4	3.625	0.472
July	4	2.375	0.640	4	4.725	0.250	4	3.825	0.472
August	4	3.025	0.350	5	5.300	0.745	4	4.675	0.492
September	4	4.600	0.497	3	4.967	0.751	4	5.000	0.346
October	4	5.175	0.550	4	5.950	0.252	4	5.125	0.096
November	4	5.200	0.668	5	4.580	0.973	5	5.540	0.404
December	5	7.520	0.432	4	5.375	0.550	4	6.425	0.287

Let S_h be the true variance in the h stratum and let y_h be the stratum mean based on a sample of size n_h. Let n represent the total sample size for the region. Then the estimate of the region mean is given by

$$y = \Sigma(N_h/N)y_h$$

It is suggested that proportional allocation be used in each stratum. This implies that $n_h/n = N_h/N$. In this case, the estimate of variance in the sample mean is given by

$$V(y) = 1/n\ (1-n/N)\ \Sigma w_h S_h^2$$

where $w_h = N_h/N$ representing the stratum weight. It can be estimated by means of other measures of relative size.

The proportion of lakes to sample in each stratum as a function of the total sample size can be calculated by proportional allocation. It is important to note that the variance in each stratum, or at least an estimate of it from a pilot study, must be known. It was assumed that each lake was sampled once insofar as the plan was concerned. Of course, it is possible to take into account more frequent sampling of the same lake.

Having determined the relative frequency of sampling in each stratum, it is now essential to determine the total sample size n. There are two distinct ways of doing this. Assuming n/N is very small, n can be chosen so as to guarantee a confidence level of $(1-\alpha)$ for detecting a change of size d from the region mean. Setting $\sigma^2 = V(y)$, and z = the upper $100(1-\alpha)\%$ point of a standard Gaussian distribution, then

$$n = z^2\sigma^2/d^2$$

Alternatively, n may be chosen to take into account the sampling costs. If the cost of taking a sample in the h stratum is c_h and the overhead cost is a, then the total cost function is

$$C = a + \Sigma c_h n_h$$

An optimal allocation scheme that minimizes the variance of y subject to the cost constraint gives

$$n_h/n = (N_h S_h/c_h)/(\Sigma N_h S_h/c_h)$$

and

$$n = (C-a)(\Sigma N_h S_h/c_h)/(\Sigma N_h S_h/c_h)$$

This procedure was used to verify that the lake sampling design in Nova Scotia, Newfoundland, and Quebec was adequate given the objective of detecting a 10% change in the mean. Data from Harp Lake were used to estimate the values needed for this calculation. The results are shown in Section 4.0. When sufficient data to determine the actual values within a region have been collected, these calculations will be reworked and any necessary adjustments to the sampling program will be made.

3.2 Surface Waters

3.2.1 *Conceptual Approach and Selection of Monitoring Areas*

Locations for LRTAP aquatic effects monitoring were selected by determining the sensitive regions or areas across the country and then identifying where these most sensitive regions coincided with the highest levels of acid deposition. Figure 1 shows the potential of soils and bedrock to reduce the acidity of atmospheric deposition in Canada and also the isopleths for wet deposition sulphate loadings in kilograms per hectare per year. The locations of these isopleths can vary from year to year depending on the variability of the annual weather pattern. Because of the presence of windblown calcium sulphate dust in parts of western Canada, these isopleths may not accurately reflect the actual deposition for these regions. The isopleths shown are for 1980 and are to be used only as a guide. A highly sensitive area with a high acid loading should be considered as a location where aquatic systems are most likely to be affected; therefore these areas should receive the highest priority for monitoring. Other sensitive areas with lower loadings should also be monitored to provide control information.

The present control strategy for the Canadian LRTAP program is to reduce levels of sulphate in wet deposition to 20 kg/ha per year or less. It is estimated that this level will protect all but the most sensitive aquatic systems by ensuring that mean annual pH levels remain ≥5.3 (Memorandum of Intent, 1983). Therefore, sensitive areas located in regions receiving an annual sulphate in wet deposition loading of >20 kg/ha per year are considered to be the most important for monitoring purposes. Because of yearly variations in deposition, however, all areas receiving sulphate in wet deposition of ≥10 kg/ha per year are considered important.

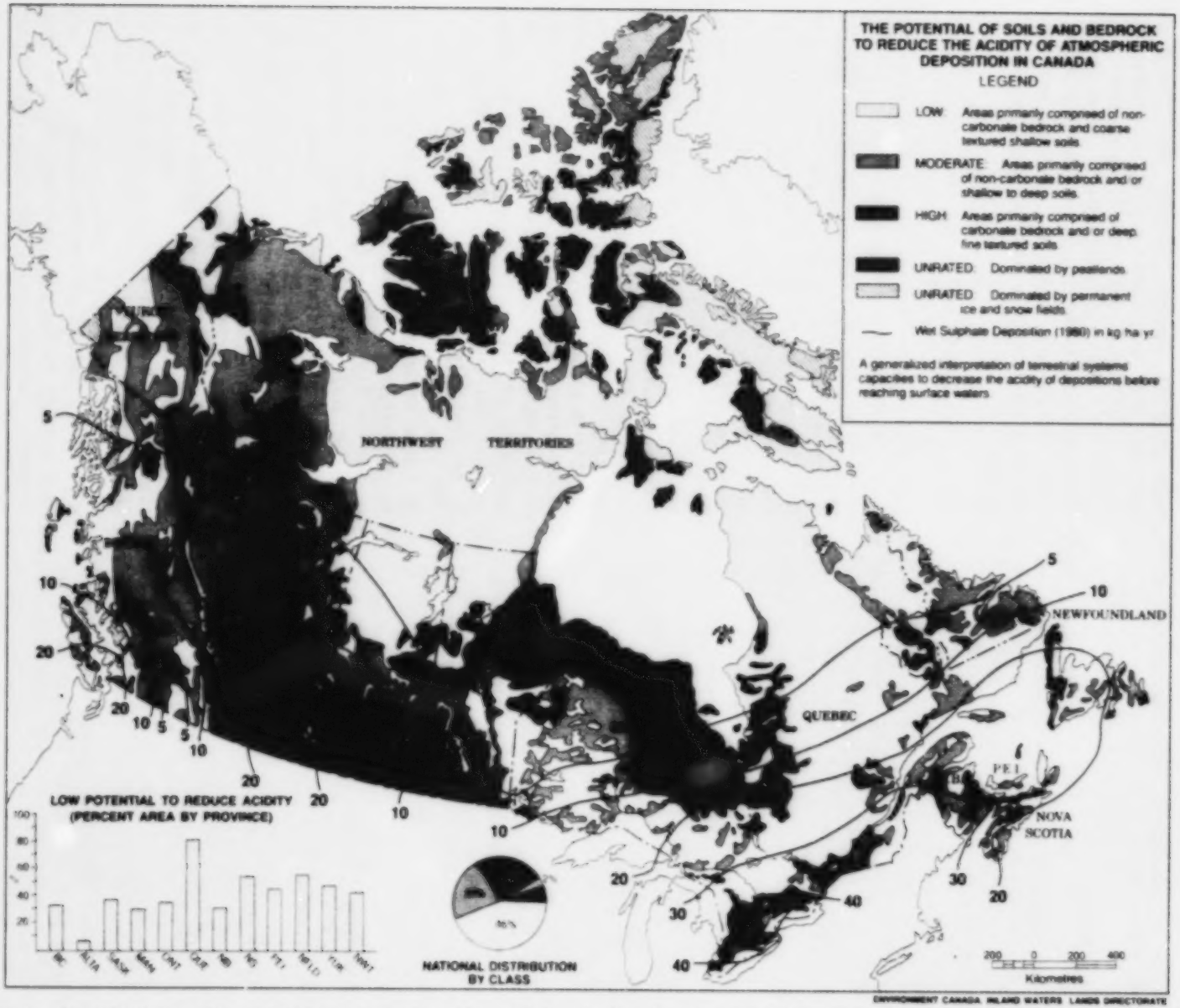
THE POTENTIAL OF SOILS AND BEDROCK TO REDUCE THE ACIDITY OF ATMOSPHERIC DEPOSITION IN CANADA
LEGEND
LOW: Areas primarily comprised of non-carbonate bedrock and coarse textured shallow soils
MODERATE: Areas primarily comprised of non-carbonate bedrock and or shallow to deep soils
HIGH: Areas primarily comprised of carbonate bedrock and or deep, fine textured soils
UNRATED: Dominated by peatlands
UNRATED: Dominated by permanent ice and snow fields
Wet Sulphate Deposition (1980) in kg ha yr
A generalized interpretation of terrestrial systems capacities to decrease the acidity of depositions before reaching surface waters
NORTHWEST TERRITORIES
QUEBEC
NEWFOUNDLAND
NOVA SCOTIA
PEI
LOW POTENTIAL TO REDUCE ACIDITY (PERCENT AREA BY PROVINCE)
NATIONAL DISTRIBUTION BY CLASS
Kilometres
ENVIRONMENT CANADA INLAND WATERS LANDS DIRECTORATE

Figure 1. Potential of soils and bedrock to reduce the acidity of atmospheric deposition in Canada and deposition of sulphate in wet precipitation (kg/ha per year).

The monitoring strategy employed here is based on dividing the country into three zones according to annual sulphate load via wet deposition. Figure 2 shows these three zones. Zone I is the most important; it includes all areas receiving 10 kg/ha per year SO_4^{2-} in wet deposition and must receive the highest priority monitoring. Zone II includes areas receiving between 5 and 10 kg/ha per year of SO_4^{2-} in wet deposition and is of secondary importance. Zone III includes all areas receiving less than 5 kg/ha per year of SO_4^{2-} in wet deposition. Within each zone, areas having moderate to high sensitivity will be monitored.

In western Canada, where the levels of sulphate in wet deposition are generally lower than 10 kg/ha per year, a lower target loading level may be established to prevent future degradation of the environment from its present state. If a lower target loading is adopted, this plan will need to be revised accordingly.

Within Zone I, the sensitive regions within the following areas are proposed for monitoring:

(a) insular Newfoundland

(b) southern Nova Scotia

(c) southwest New Brunswick

(d) Quebec North Shore to Lac St. Jean

(e) Quebec Lac St. Jean to Outaouais region

(f) central Ontario (Dorset, Haliburton)

(g) Ontario Algoma region

(h) Ontario Quetico/Thunder Bay region

(i) British Columbia Pacific coast

Sites in these areas should be monitored at a minimum frequency of twice a year.

Within Zone II, selected lakes in each of the following areas should be monitored once every three to five years:

(a) Labrador

(b) Quebec

(c) northwestern Ontario

(d) northern Saskatchewan

Twelve lakes from the Experimental Lakes Area in northwestern Ontario (Zone II) will be sampled annually. These data will be used as a control for the monitoring network.

For Zone III, which comprises northern Quebec and large areas of the Northwest Territories and the Yukon Territory, it is recommended that a lake sensitivity study be carried out to improve the definition of the present status. If in the future there are indications from results in Zones I and II that changes are occurring, then a repeat sampling should be carried out to determine if similar changes have taken place in the northern regions. No fixed or recurrent monitoring program is justified at the present time in these regions.

Section 4.0 describes the implementation of this monitoring network and the techniques used to select the monitoring sites within the areas selected for monitoring. Appendices A and B give more detailed information about monitoring in the Atlantic and Quebec regions.

3.2.2 *Siting Criteria (Rivers and Lakes)*

The sites selected should be representative of the aquatic resources of the region. Data describing the aquatic resources are available from prior surveys and are contained in NAQUADAT. Information for siting of sampling stations was obtained by analyzing these data by statistical methods and interpreting the results according to the sensitivity of the regions to acidification. Criteria that have been used as guidance in site selection are as follows.

The individual sites chosen should not be affected by local emission sources or anthropogenic activities such as logging, mining, farming, or other disruptive land use activities either in the present or in the foreseeable future, and preferably not in the past as well. Sites in national or provincial parks, where some measure of protection against future human activities can be assured, should be considered.

The following siting criteria should also be considered:

(a) sites where historical data are available;

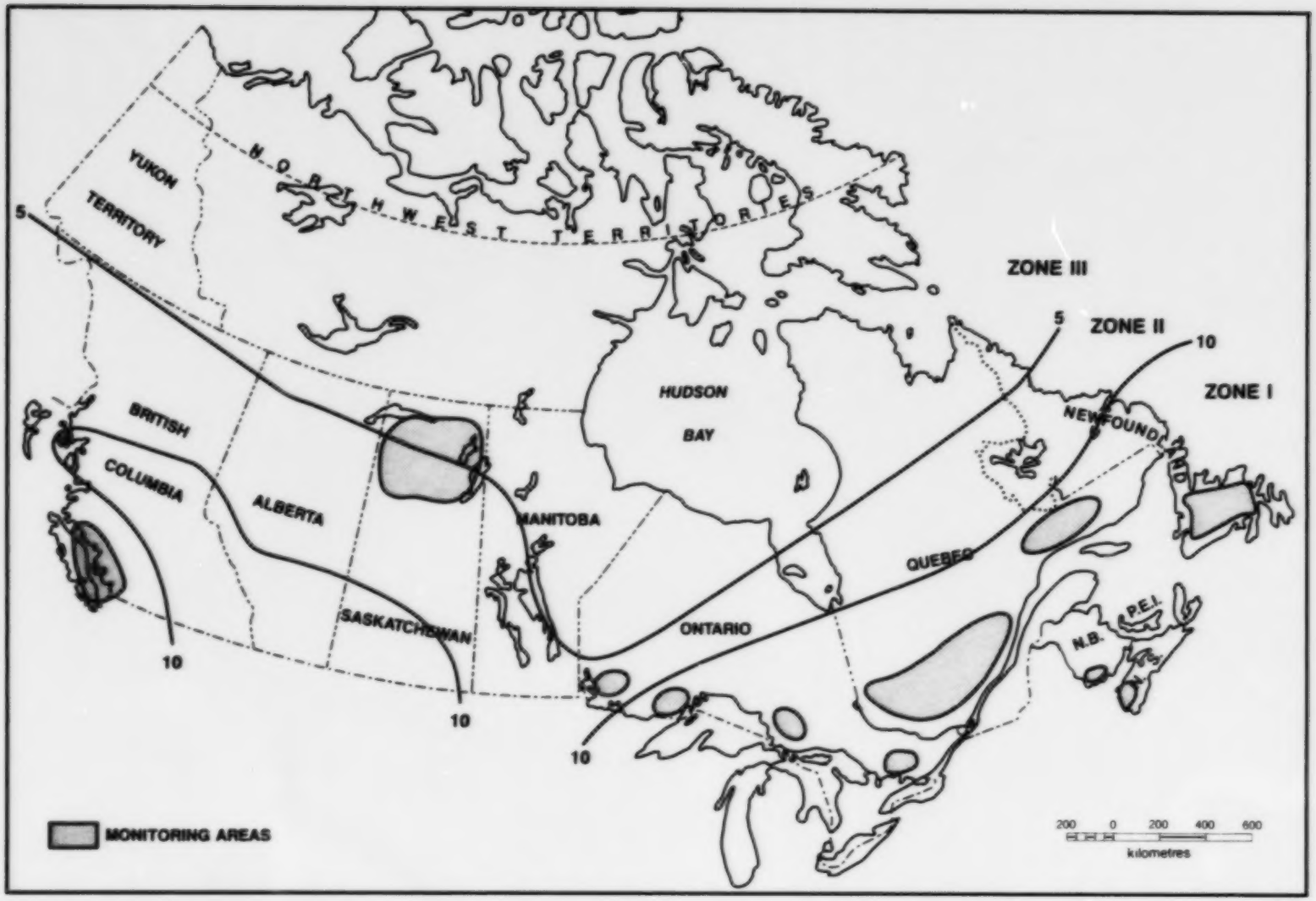

Figure 2. Suggested areas for monitoring aquatic effects of acid deposition. (Isopleths show sulphate concentration (mg/l) in wet deposition.)

(b) sites where research activities can provide additional information;

(c) sites close to deposition monitoring sites;

(d) sites on rivers or streams that are gauged;

(e) sites where the river or stream is well mixed to provide a uniform concentration profile for a given segment or reach;

(f) sites that are easily accessible.

3.2.3 *Site Documentation and Characterization*

The following information should be compiled and made available for all surface water monitoring sites (i.e., lakes, rivers):

(a) name of the river or lake

(b) boundaries or segment sampled

(c) location, universal transverse Mercator coordinates, or latitude and longitude

(d) water depth at the site

(e) altitude of the site above sea level

(f) area of the watershed

(g) morphometric measurements of lakes (surface area, maximum depth, mean depth, and volume)

(h) bedrock geology of the basin

(i) soil classes in the watershed/aquifer

(j) historical, existing, and anticipated land use in watershed

(k) past and anticipated land disturbances in the watershed (i.e., forest fires, road construction, etc.)

(l) presence and description of inflowing and outflowing streams to the lake

(m) water residence time in lake, if known

(n) hydrologic lake type; linkage to other surface waters

(o) description of any known pollution sources (old mine workings, etc.) that may affect the water body

(p) topographic map showing site location

The above information will be compiled and maintained in report form for each monitoring site. To further characterize these basins, samples of media (i.e., soil, sediments, biota, etc.) other than those being monitored under this program will be collected and analyzed to determine such characteristics as acid neutralizing capacity and food chain components. Other agencies will be solicited to assist in these tasks.

3.2.4 *Parameters to be Measured and Recommended Methods*

The following core measurements will provide sufficient information to make assessments of the sensitivity and changes in water quality related to acidification.

pH. pH is a measure of the hydrogen ion concentration in solution and can be considered a direct indicator of acidification. It is recommended that both field and laboratory measurements of pH be taken.

Alkalinity. Alkalinity is a measure of a water's capacity to neutralize an acid. It indicates the presence of carbonates, bicarbonates, and hydroxides, and less significantly, borates, silicates, phosphates, and organic substances. The Gran method is recommended for low alkalinity waters. Alkalinity is one of the major indicators of the sensitivity of the system to acid loading. Table 1 shows a system for classifying lakes according to their sensitivity to acid rain using alkalinity or ANC as the indicator.

Specific conductance. Specific conductance gives a measure of the ionic concentration of the dissolved minerals. Conductance has been used as an indicator of sensitivity towards acid loading, i.e., the lower the conductance, the more sensitive the water body is to acid precipitation. It is usually measured by a conductance meter based on the Wheatstone bridge. The measured conductance is then corrected to the specific conductance at 25°C.

Major ions. All major ions concentrations are necessary for the LRTAP program. The cations

are an important measure of the geochemical weathering processes and are used as the primary measure of sensitivity to acidification. Sulphate and nitrate ions are components of the deposition. Sodium and chloride ions are necessary for calculating sea salt corrections in areas under a marine influence. These major ions, together with alkalinity, are all necessary to perform cation/anion balance calculations. This is an important check on data quality. Recommended analytical methods are atomic absorption spectroscopy for calcium and magnesium, flame photometry for sodium and potassium, ion chromatography for sulphate, and the automated mercuric thiocyanate for chloride.

Colour. Colour can often be an indicator of the presence of organic matter, such as humic and fulvic acids, tannins, and lignins in the water. These compounds have the ability to complex metals (e.g., aluminum) that are solubilized at lower pH levels, thus reducing the metals' toxic effects. Organic acids are also a source of natural acidity. Colour in a sample is determined by visual comparison with known concentrations of coloured solutions of chloroplatinate ions.

Aluminum. At lower pH levels, aluminum solubility in water increases and more aluminum is leached from soils and sediments. In the monomeric form, aluminum can have a toxic effect on aquatic biota. Although monomeric aluminum is the preferred form to be measured analytically, the separation techniques are time-consuming and expensive. For the present, it is recommended that dissolved aluminum and total aluminum should be measured.

Dissolved inorganic carbon (DIC). Dissolved inorganic carbon is a measure of the sum of the carbonates, bicarbonates, and carbonic acid present in the water. This parameter is useful as a check on the alkalinity measurements. Dissolved inorganic carbon is usually measured using an infrared (IR) analyzer. The sample is acidified after filtration through a 0.45-µm membrane filter. The resulting carbon dioxide is stripped from solution and measured by an IR analyzer.

Dissolved organic carbon (DOC). Dissolved organic carbon is a measure of the organic material dissolved in the water. These materials contribute to the water colour and also to the natural acidity system. Dissolved organic carbon is measured using an IR analyzer. After filtration the sample is acidified to convert inorganic carbon to carbon dioxide, which is stripped from solution. The remaining liquid phase is passed through a UV coil to oxidize organic carbon compounds. The resulting carbon dioxide is measured by an IR analyzer.

Flow. Water discharge measurements (or the ability to estimate flow measurements) are essential for determining the flux of a material in dissolved form carried by a river out of a basin.

Measurements for the following, while not essential, would provide additional information to aid in data interpretation: iron, manganese, zinc, copper, nickel, lead, silica, fluoride, total phosphorus, total Kjeldahl nitrogen, ammonium, and dissolved oxygen. In lakes chosen for biomonitoring, additional chemical measurements may be required (e.g., nutrients).

3.2.5 *Frequency of Sampling*

3.2.5.1 Lakes

If only the year-to-year change is required, and the within-year variability is to be disregarded, then it is acceptable to sample in the fall after turnover, when the lake is well mixed, and to compare these data from year to year. Sampling at this time of year is recommended for the recurrent lake monitoring. For a given lake, however, it takes a long time to obtain a data set large enough to perform a meaningful data analysis.

If knowledge of the temporal variability over a given year is required, then the following strategy is recommended. The lakes should be sampled at least six times a year, ensuring that samples are collected to cover the following periods: during open water prior to summer stratification, during summer stratification, during mixing following summer stratification, under ice, and during the period of snowmelt and runoff.

For LRTAP aquatic effects monitoring, a combination of the above two approaches is recommended. By sampling a small number of lakes more frequently, the temporal objectives of the network will be met. This information can be extrapolated over a much larger area by sampling additional lakes at a much reduced frequency. This will address the spatial concerns of the network.

The procedure recommended is as follows. Using the data from the lake surveys, cluster the lakes into groups using pertinent water quality and basin variables. Then select a small number of lakes (5 to 7) from each group for annual sampling. One or two of these lakes should be sampled 6 to 12 times a year and the remainder twice a year. Those sampled intensively would be sampled at least during the periods mentioned above. Those sampled twice a year would be sampled while the lakes are thermally homogeneous, that is, during open water prior to summer stratification and after mixing following summer stratification.

Sampling in this manner will provide the most useful data in the most efficient manner and is the recommended sampling scheme for lakes that have been grouped.

In any event, the adequacy of a sampling plan for a given sensitive region depends on N the number of samples collected in the region. N is a function of the number of sampling sites times the frequency of sampling. The size of N required can be determined statistically and will vary from region to region and will depend on the area and physico-geographic characteristics of the region.

3.2.5.2 Rivers

Rivers should be sampled more frequently than lakes because of the greater temporal variability in the chemical composition of their waters. Sampling should be carried out over the range of discharge using a stratified random sampling approach, i.e., more samples will be collected during the periods of greater variability in flow. It is recommended that at least 12 samples be collected every year.

3.3 Ground Waters

3.3.1 *Selection of Monitoring Areas and Siting Criteria*

For ground-water monitoring, only areas subject to high loading and having a terrain sensitive to acid deposition should be considered (i.e., the worst case). The rationale for this is that, unlike surface waters, ground waters are in contact with soil particles for longer periods of time because of their slower flow rates. Thus even in the most sensitive ground-water systems, this contact time with the soil particles permits some measure of buffering against the acidity. Given this buffering capacity, it is expected that changes in ground-water chemistry brought about by acid deposition will take place at extremely slow rates.

A typical ground-water monitoring site will have the following characteristics. It will be located in one of the areas of sensitive terrain within Zone I as shown in Figure 2. The aquifer chosen will be shallow and have a short flow path (less than 5 years). The monitoring sites will be located in the recharge and discharge areas of this flow path and will be accessible by road or closely linked to a surface water site. They should be removed from all local sources of pollution. An existing site having a historical data set would be preferred.

3.3.2 *Site Documentation and Characterization Requirements*

The following information should be compiled and made available for all ground-water monitoring sites:

(a) name of the well

(b) location, universal transverse Mercator coordinates, or latitude and longitude

(c) bedrock geology

(d) soil classes in the aquifer

(e) historical, existing, and anticipated land use in the area

(f) past and anticipated land disturbances in the area

(g) description of any known pollution sources

(h) topographic map showing site location

(i) permeability

(j) depth of unsaturated zone

(k) depth of well

(l) length of screen

(m) diameter of well

(n) hydraulic head

The above information will be compiled and maintained in report form for each monitoring site.

3.3.3 *Variables Measured*

The variables measured in ground water are similar to those recommended for surface water monitoring with the addition of the field measurements. These are temperature, pH, redox potential, specific conductance, and dissolved oxygen. The pH, dissolved oxygen, and redox potential measurements must be made using a flowcell.

Nitrate, nitrite, and ammonium ions should also be measured. While concentrations of these ions are usually very low in the surface waters of interest to the LRTAP program, higher concentrations can exist in ground water. Ammonia is measured by a colorimetric autoanalyzer method using o-tolidine.

Nitrate and nitrite values can be determined by the automated cadmium reduction technique. The nitrates are reduced to nitrites by the cadmium. The resulting nitrites plus those already present react then with sulphanilamide to form the diazo compound and hence the azo dye, which is measured colorimetrically.

Separate nitrate and nitrite values can be obtained by carrying out the procedure without the cadmium reduction step.

3.3.4 *Frequency of Sampling*

Ongoing research indicates that a frequency of 6 to 12 samples a year should result in adequate coverage. This frequency is compatible with that of other networks: Finland (6 to 12 a year), Norway (2 to 3 a year), Sweden (2 to 6 a year), and Iceland (2 to 12 a year) (Eernes, 1980; Nordberg, 1980). The majority of these samples will be collected in the snow-free period on a schedule compatible with other activities of the monitoring network.

4.0 IMPLEMENTATION OF THE AQUATIC EFFECTS MONITORING PROGRAM

In response to the urgency of the request and the importance placed on this monitoring program, sites have been selected and sampling has commenced in a number of sensitive areas. The majority of the sites selected for LRTAP aquatic effects monitoring were already included in other monitoring or research programs and fulfilled the siting criteria, or were sampled during one of the many lake surveys carried out in eastern Canada.

This section gives a brief description of the present status of the monitoring actually under way for each of the areas mentioned in Section 3.2.1. Appendices A and B give a more detailed description of the monitoring programs in the Atlantic and Quebec regions.

4.1 Atlantic Region

LRTAP aquatic effects monitoring in the Atlantic Region (AR) comprises river and lake monitoring sites. Twenty-seven rivers from the four provinces were chosen and are monitored by WQB-AR. These rivers have been sampled regularly for 10 years or more, and much historical water quality data exist. In addition, many of these rivers provide spawning grounds for Atlantic salmon (*Salmo salar*). The rivers are sampled 12 times a year.

The lakes chosen for monitoring were selected from a large inventory initially surveyed by Environment Canada, Fisheries and Oceans Canada, and various provincial agencies. The lakes were divided into two groups: one for Newfoundland and one for Nova Scotia. For each area, the lakes were clustered into groups and a small number of lakes selected from each group based on the common characteristics from the cluster analysis.

Forty-four lakes were selected in southern Nova Scotia and 34 in Newfoundland. These lakes are sampled twice a year, in the spring and fall. To verify that sufficient samples are being collected, the data from Harp Lake, Ontario, were analyzed to determine the annual variabilities (Table 2) for alkalinity and sulphate. This data set collected by the Ontario Ministry of the Environment was the only long-term lake data set available at the time. These variabilities were used along with the procedure described in Section 3.1 to verify that the number of samples collected in these two regions is adequate. Table 5 shows the results.

Table 5. Number of Water Samples Required Each Year from the Lake Network to Detect a Change in the Levels of Alkalinity and Sulphate at 95%, 90%, and 80% Confidence Levels

Confidence level (%)	Alkalinity increment (mg/L) 0.5	1	1.5	SO_4 increment (mg/L) 0.5	1	1.5
Southern Nova Scotia (N = 88)						
95	39	10	5	61	16	7
90	33	9	4	51	13	6
80	26	7	3	40	10	5
Newfoundland (N = 70)						
95	76	19	9	120	30	14
90	53	14	6	84	21	10
80	33	9	4	51	13	6

Eighty-eight samples a year are collected for Nova Scotia. At a 90% confidence level 33 and 51 samples are required to detect a change in concentration of 0.5 mg/l for alkalinity and sulphate. The sampling plan for this sensitive region is adequate. In Newfoundland, however, where WQB collects 70 samples a year, the results indicate that 84 samples are required to detect a 0.5 mg/l change in sulphate concentration with a confidence level of 90%. Additional water samples collected by Fisheries and Oceans Canada as part of its biomonitoring program make up this shortfall. No further effort is required on the part of WQB.

The sensitive areas in New Brunswick are sampled by the province and by Fisheries and Oceans Canada. However, the sampling frequency, which is a recurrent monitoring on a five-year cycle, should be increased. This increase will require additional resources.

A survey of lakes in Labrador (Zone II) was carried out in 1981. A subset of these lakes, selected by clustering analysis, should be resampled every five years.

4.2 Quebec Region

Thirty-six lakes in the Quebec Region are sampled by IWD. These include Lac Laflamme, which is in a research study basin and is sampled weekly. The remaining 35 lakes are located north of the St. Lawrence River between the Ottawa and Saguenay rivers. They were selected by using clustering analysis to group 185 lakes that had been surveyed to determine the aquatic sensitivity of the region. (See Appendix B for more detailed information.) There are five groups of lakes. Two lakes in each group are sampled six times a year, and the remainder, two times a year. Sampling commenced in 1983.

An additional cluster of approximately six lakes in the Abitibi/Temiscaming region will be added to the network. Some lakes along the North Shore will be chosen, and sampling will commence when resources are available.

The IWD monitoring program along with the complementary programs operated by Environnement Québec and the Department of Fisheries and Oceans will complete the LRTAP aquatic effects monitoring requirements for the province.

Environnement Québec is monitoring 337 lakes each year over a five-year cycle. This large number of lakes will permit a better definition of the status of lakes over a much greater area than that covered by the IWD-monitored lakes.

Fisheries and Oceans Canada is monitoring a number of important salmon rivers along the Quebec North Shore.

The calculations that were applied to the lakes in the Atlantic Region to determine the adequacy of the sampling program were also applied to the IWD lakes in Quebec. Results showed that the sampling program was adequate to detect the required incremental changes in the values of alkalinity and sulphate concentrations for the region covered by the 36 lakes.

4.3 Ontario Region

Three sensitive regions in Ontario (located in Zone I) have been identified for LRTAP aquatic effects monitoring. These are Ontario central region (Dorset, Haliburton), Algoma region, and the Boundary Waters Canoe Area/Thunder Bay region. The

Ontario Ministry of the Environment (MOE) samples lakes in the Dorset area as part of its research studies, and large amounts of data exist for these sites.

The Algoma region north of Sault Ste. Marie is the location of the IWD/DFO Turkey Lakes Basin Studies. A large data base has been accumulated for four lakes (Turkey Lake, Little Turkey Lake, Wishart Lake, and Batchawanna Lake). Sampling continues at these sites on a weekly basis. In addition, DFO has surveyed many lakes in the region. The Canadian Wildlife Service has sampled more than 100 lakes for three consecutive years in the vicinity of Ranger Lake, located about 50 km south of the Turkey lakes. Lake surveys have also been carried out in Pukaskwa National Park about 160 km northwest of the Turkey lakes.

The monitoring network in this region will include the three lakes in the intensive study basins and other lakes in the region to be selected from the lakes already surveyed. Lakes in Pukaskwa National Park should be considered because of the protection against future disturbance by anthropogenic activities.

A group of lakes should be selected and monitored in the Quetico area west of Thunder Bay, Ontario. These lakes would provide a comparison to the lakes in northern Minnesota monitored by the United States Environmental Protection Agency. The Ontario Ministry of the Environment has surveyed many lakes in this area, and it is expected that it will carry out this monitoring.

For the most part, lakes in northwestern Ontario, although highly sensitive to acidic deposition, are in a Zone II region because of the low atmospheric loading of acidic materials.

In place of recurrent monitoring, a group of lakes in this region have been selected for annual monitoring and have been designated as a control for the monitoring network. These lakes are located at the Experimental Lakes Area study site near Kenora, Ontario. The research site is operated by Fisheries and Oceans Canada and is used for lake manipulation studies. The 12 lakes included in the monitoring network are the lakes designated as control lakes for the research studies. Much water quality data and basin information already exist. The lakes are sampled annually, although the frequency can vary from lake to lake and year to year. To date the frequency has been adequate.

4.4 Western Canada

With the exception of the coastal region of British Columbia north of Vancouver, the sensitive regions of western Canada are all in a low loading zone and include the Shield areas of northern Manitoba and Saskatchewan and parts of the Northwest Territories.

At present the only IWD LRTAP aquatic effects monitoring in western Canada is the joint Water Quality Branch/Saskatchewan Environment monitoring project in northern Saskatchewan. Twenty-two lakes in the Shield area of northern Saskatchewan have been selected for monitoring. A further six lakes in the vicinity of the Cree Lake deposition monitoring station were selected for more intensive study and sampled in 1986/87. When sufficient data are available, the results will be reviewed to determine whether an annual or recurrent monitoring program should be established for the Shield areas of northern Saskatchewan and northwestern Manitoba.

LRTAP aquatic effects monitoring is being carried out in the Pacific coast region of British Columbia by both B.C. Environment and Fisheries and Oceans Canada. Some of the B.C. Environment monitoring sites are included in the federal/provincial water quality agreement. There are no plans for IWD participation in the sampling programs at the present time.

Large areas of the Northwest Territories and the Yukon Territory have been identified as highly sensitive to acid deposition. These assessments are based on sparse water quality data. These data must be reviewed and a sampling of lakes in these areas must be carried out to improve the definition of the sensitivity maps and to provide baseline data.

5.0 DATA MANAGEMENT

It is essential that all monitoring data be stored in a central data bank for control and coordination. Having the data available in a similar format will greatly assist the data analysis and interpretation as well as allowing a composite view of all the monitoring programs.

Data from the samples submitted to the laboratory for analysis will be returned to the agency or regional office responsible for carrying out the sampling program. Here, these data will be merged with the data collected in the field and verified for accuracy. Results from the quality assurance samples will be used for this purpose (Section 6.0).

When verified, the data will be forwarded to the National Water Quality Data Base (NAQUADAT), directly in the case of IWD regional offices or via the agency's own data archiving system. The time lapse between sampling and data entry onto the NAQUADAT system should be no greater than six months.

NAQUADAT will assume responsibility for storing and maintaining the archive. As part of this service, data will be made available to requesting agencies or researchers on magnetic tape, computer printouts, or via telecommunication facilities. The entire range of NAQUADAT reporting and graphical facilities will be available for analyzing and interpreting the accumulated data.

6.0 QUALITY ASSURANCE

A good quality assurance program is essential for verifying the accuracy and precision of each activity in the operation of the network. The quality assurance program should address field procedures, laboratory analysis, and data management.

Appendix C gives a series of recommended procedures for the collection and analysis of water samples. There are, however, a variety of acceptable methods in use by the various agencies. This makes it imperative that a quality assurance program be used by all agencies to ensure the accuracy and comparability of the data produced.

6.1 Field Procedures

Field procedures are often the weakest component of the network operation. The variety of techniques in use, poor documentation, and a lack of adequate quality control checks are responsible in many cases for the lack of confidence in the historical water quality data.

Gaskin and Watt (1987) detail and recommend the various quality control checks that can and should be used in a field quality assurance program. A minimum program should consist of triplicate sampling and field blanks.

6.2 Laboratory Analysis

Quality assurance of laboratory analysis has been well studied, and most modern laboratories have adequate quality control programs. A document prepared for the LRTAP quality assurance and methods subgroup (Ad-Hoc Work Group on Quality Control, 1983) details the procedures to be followed in setting up a laboratory quality assurance program. All laboratories analyzing water samples for the LRTAP aquatic effects monitoring network take part in the Laboratory Quality Control Program operated by the National Water Research Institute (NWRI), Burlington, Ontario.

6.3 Data Management

All data from the field and laboratory should be sent (after verification at the source) to a central data bank (NAQUADAT). The data should be submitted to various editing and balancing checks before being stored in the data bank. The data bank should archive all pertinent documentation about the monitoring sites, basins, and techniques used for the sample collection and analysis.

7.0 DATA ANALYSIS AND INTERPRETATION

Data analysis and interpretation will be performed at two levels: regional and national. At the regional level, the data-collecting agency or agencies will analyze the data for changes and trends within the region. The data will also be compared to regional deposition levels and other observed effects within the region. The regional information will then be compiled into a single national report documenting the annual status of aquatic resources in Canada with respect to acid deposition. Regional changes or trends observed will be compared across Canada.

The data collected will also be used, together with models developed by researchers, to estimate future changes. This information can then be used to assess the effectiveness of controls or remedial programs and suggest modifications where necessary.

The analysis and interpretation of the data will also serve in the evaluation of the monitoring network, e.g., whether or not additions or deletions of stations or parameters, and changes in sampling frequency are required.

8.0 REPORTS AND REPORTING SCHEDULE

The following reports will be prepared:

(a) Aquatic baseline report. This report will document the present status of Canada's aquatic resources with respect to acidification-related parameters. It will be restricted to surface water chemistry variables.

(b) Site documentation. This report will be a compendium of the LRTAP monitoring sites and the information compiled relative to those sites.

(c) Annual status reports. Commencing the year after publication of the aquatic baseline report, these reports will compare the past year's monitoring data to the baseline report and previous monitoring data. Any changes or trends detected will be documented.

(d) Data summaries. These reports will be produced periodically for distribution to agencies or individuals who do not have access to the interactive data system.

9.0 REFERENCES

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Appendix A
LRTAP Aquatic Effects Monitoring—Atlantic Region

APPENDIX A

LRTAP AQUATIC EFFECTS MONITORING–ATLANTIC REGION

A.1 INTRODUCTION

The Atlantic provinces include all the areas east of Quebec, i.e., New Brunswick, Nova Scotia, Prince Edward Island (P.E.I.), and Newfoundland and Labrador. They include ecotypes as diverse as hardwood forests and shrub-lichen heaths.

The bedrock geology of the region is complex. From an acid precipitation standpoint, a number of zones are important. Southwest Nova Scotia, as well as Cape Breton, contains large regions of granites, as well as siliceous sediments containing shales with no buffering capacity. Much of Newfoundland and Labrador also contains the same types of bedrock (Shilts, 1981). New Brunswick and P.E.I. are underlain with sandstones of moderate buffering capacities. In both the sensitive areas of Nova Scotia and Newfoundland, soils are mostly thin and podzolic, providing little neutralizing capacity (Rubec, 1981).

The area receives precipitation with pH ranging from 4.3 in extreme southwest Nova Scotia to 4.9 in Labrador (Atmospheric Environment Service, 1980) (Table A-1). Shaw (1979) reports that the anthropogenic sulphate deposited in Nova Scotia originates in the eastern seaboard states, the Ohio Valley, the Great Lakes area, and Ontario, as well as from some local sources.

Table A-1. Volume-Weighted Means at Regional CANSAP Stations in 1980

Station	pH	SO_4^{2-} (μ moles.l^{-1})
Shelburne, Nova Scotia	4.3	16
Kejimkujik, Nova Scotia	4.5	15
St. John, New Brunswick	4.2	22 (local influence)
Charlo, New Brunswick	4.8	22 (local influence)
Gander, Newfoundland	4.8	22 (local influence)
Goose Bay, Newfoundland	4.9	9

Due to their low buffering capacity and the hydrogen and sulphate ions deposition, the surface waters in a number of basins of the Atlantic provinces are more acidic than would be expected under pristine conditions. Clair *et al.* (1982) show the distribution of pH levels for the region and support the fact that the most poorly buffered areas contain waters of low pH.

A factor complicating the interpretation of low pH waters is the presence of naturally produced organic acids from the podzolic soils and bogs that leach into lakes and rivers and tend to depress water pH when at high enough concentrations. The Atlantic region has a high proportion of these waters, and any data analysis has to take this factor into consideration. Despite the natural acids, however, strong evidence suggests that acidification is a major problem at least in southwestern Nova Scotia. Watt *et al.* (1983) have shown that Atlantic salmon *(Salmo salar)* populations in the region have suffered a serious decline over the last 20 years, and that this decline corresponds to apparent increases in river acidity.

The following describes the monitoring plans for both rivers and lakes in sensitive basins of Atlantic Canada, how these have been set, and what results have been noted up to now.

A.2 RIVERS

The Water Quality Branch, Atlantic Region (WQB-AR), and its predecessors have been involved in the monitoring of river quality since the mid-1950s with water quality surveys for industrial uses (Thomas, 1960). With its involvement in the International Hydrological Decade (IHD), WQB-AR sampled a number of rivers from all provinces on a regular basis for almost ten years. This program ended in the mid-1970s, but the accumulated data base formed the basis for the selection of rivers for aquatic effects monitoring.

Twenty-eight rivers from the four provinces were chosen from information contained in the data base (NAQUADAT). Following are the criteria used in the selection.

(a) Previous data record. (This allows for long-term comparisons.)

(b) Minimal human disturbance. (This does not preclude new level logging or small farms.)

(c) Well-mixed rivers and streams. (There should be enough turbulence to break down any stratification.)

(d) Rivers and streams have to be gauged.

(e) The basin should be sensitive to acidification based on Clair *et al.* (1982).

One criterion was not strictly followed: the

Table A-2. Water Quality Branch River Monitoring Sites

NAQUADAT No.	Name	Latitude	Longitude
00NS01EE0001	Medway River	44°10'26"	64°39'37"
00NS01EC0005	Roseway River	43°50'17"	65°22'10"
00NS01EA0001	Tusket River	43°55'23"	65°52'00"
00NS01EN0002	Liscomb River	45°00'47"	62°05'53"
00NS01EF0002	LeHave River	44°26'48"	64°35'30"
00NS01EB0001	St. Marys River	45°10'26"	61°58'49"
00NS01DE0001	Avon River at power dam	44°52'54"	64°13'23"
00NS01DL0009	Kelley River	45°35'12"	64°27'06"
00NS01DN0001	Wallace River	45°40'40"	63°33'29"
00NS01DA0001	Meteghan River	44°13'00"	66°07'13"
00NS01ER0001	Clam Harbour River	45°28'00"	61°27'42"
00NS01ED0005	Mersey River	44°26'12"	65°13'23"
00NS01ED0030	Rodgers Brook	44°24'50"	65°13'41"
00NS01EE0015	Whiteburn Brook	-	-
00PE01CA0001	Mill River	46°44'39"	64°10'54"
00PE01CB0001	Dunk River	46°20'44"	63°37'59"
00NB01AQ0001	Lepreau River	45°10'10"	66°28'05"
00NB01BV0015	Pointe Wolfe River	45°33'02"	65°00'47"
00NB01AN0001	Salmon River at Gaspereau Forks	46°13'48"	65°50'48"
00NB01AM0001	North Branch Oromocto River	45°40'23"	66°40'58"
00NF02ZB0001	Isle aux Morts River	47°36'50"	59°00'33"
00NF02YJ0001	Harrys River at Black Duck	48°34'32"	58°21'48"
00NF02ZH0001	Pipers Hole River at Mothers Brook	47°55'36"	54°16'27"
00NF02ZK0001	Rocky River at Colinet	47°13'31"	53°34'04"
00NF02YB0001	Exploits River at Grand Falls	48°55'50"	55°40'01"
00NF02YN0001	Indian Brook at Springdale	49°29'44"	56°05'21"
00NF02ZD0003	Grey River at WSC gauge	47°44'35"	56°56'03"
00NF02ZG0016	Garnish River	47°12'50"	55°19'45"
00NF02ZC0001	Grandy Brook	47°51'27"	57°43'59"
00NF03QC0001	Eagle River above Eagle Falls	53°27'29"	57°33'29"
00NF03BE0001	Churchill River at Muskrat Falls	53°15'29"	60°45'00"

presence of an historical record. The Grey and Cat Arm rivers in Newfoundland are in very sensitive areas and are being sampled for a better coverage despite the absence of long-term data. Table A-2 lists the rivers sampled and the location of the sampling site.

All rivers have been sampled once a month by gauge readers since 1981, except for the Grey and Cat Arm rivers, which have been sampled bi-monthly. Geological soil and plant maps are available for all basins from the Inland Waters Directorate, Environment Canada.

The selection of the rivers was based on aerial coverage as well as the presence of gauging stations and access. The frequency of sampling was based on two statistical analyses, which determined the sampling frequency needed to give trend information. Clair and Whitfield (1983), using time-series analysis on data from individual rivers for up to 12 years of monthly values, found that, generally, pH in sensitive rivers decreased over time, while sulphate and calcium did not show the expected increase.

Alvo, Clair, and Cohen (1983) have also studied the sampling frequency necessary for accurate determination of pH and SO_4^{2-} changes and have suggested a number of alternatives based on the types of results wanted and resource availability. These are under study, but the analysis shows that monthly sampling of river sites is still an acceptable frequency.

A.3 LAKES

The lakes chosen for monitoring were picked from a large inventory initially sampled by various Environment Canada agencies, Fisheries and Oceans Canada, and the Nova Scotia Department of the Environment. Lakes from Nova Scotia and Newfoundland were looked at separately. The first criterion for selection was that the lakes must be headwater lakes with a maximum basin size of 100 km^2. This criterion was sometimes extended to include lakes with interesting features. The second and third criteria, which were strictly adhered to, were that the lakes must have minimal human disturbance and be located in sensitive areas (based on Clair *et al.*, 1982).

Lakes in areas sampled are generally oligotrophic. They are mostly shallow with little stratification until the summer. Table A-3 describes thermal regimes for lakes in southwestern Nova Scotia. These data suggest that there is no serious change in parameter levels from the surface to the bottom of many lakes for at best one or two months during overturn periods. It was then decided that the lakes would be sampled only at fall and spring overturns when chemical levels in the lakes were most homogeneous. The rationale for this decision was that in a long-term monitoring program with limited resources, more information on

Table A-3. Stratification in Selected Monitored Lakes from Southwest Nova Scotia*

Lake	Max. depth (m)	Comments
Back Lake	6	Does not stratify
Big Dam West Lake	9.6	0.4% of lake volume in summer hypolimnion
Big Dam East Lake	4.2	Does not stratify
Big Red Lake	2.0	Does not stratify
Beaverskin Lake	6.3	0.3% of volume in summer hypolimnion
Coblielle Lake	6.3	Does not stratify
Frozen Ocean Lake	7.6	Does not stratify
George Lake	8.5	3.3% of volume in hypolimnion; flushing rate 319 times/year
Grafton Lake	10.5	0.1% of volume in hypolimnion
Kejimkujik Lake	19.2	Weak stratification June to August
Little Red Lake	1.3	Does not stratify
Luxion Lake	8.5	2.1% of volume in hypolimnion
Mountain Lake	14.3	Stratified mid-May to mid-October
Mud Lake	22	0.3% volume in hypolimnion
Pebbleloggitch Lake	2.5	Does not stratify
Peskawa Lake	9	0.8% volume in hypolimnion
Peskowesk Lake	13	Stratified mid-May to mid-October
Upper Silver Lake	5.8	Does not stratify

*From Kerekes, 1975, and Kerekes and Schwinghamer, 1973.

trends due to acidification could be gained when lakes presented the simplest interpretation of their chemical makeup.

Sampling is done from a helicopter, near the centre of the lake, 1 m below the surface. Metal samples are preserved in the field as soon after sampling as possible.

The lakes that were chosen for examination from the data base available were divided into two groups based on location: one in Nova Scotia and one in Newfoundland. Each group was then subjected to a clustering analysis using pH, alkalinity, sulphate, colour, chloride, and calcium. In both areas, dividing the lakes into seven groups reduced intragroup variability the most (A.H. El Shaarawi, 1986, National Water Research Institute, pers. com.). Tables A-4 and A-5 show the number of lakes chosen in each cluster and the centroid values for the parameters used in the analyses.

In Nova Scotia, lakes from all seven clusters are being sampled, while in Newfoundland, three clusters that contained lakes insensitive to acidification were not considered further. Tables A-6 and A-7 give their locations.

In Nova Scotia, the seven clusters range in size from 1 to 15 lakes, while in Newfoundland, seven lakes were picked from each group. The difference in approach is due to constraints of logistics. In Nova Scotia, the two lakes farthest from each other are 100 km apart. All the lakes that satisfy the selection criteria are then sampled and analyzed according to their clusters. In Newfoundland, however, the lakes are scattered over a 864 000-km^2 area, and so a different approach to site selection had to be taken, based on resource availability, geography, and meteorology.

Table A-4. Chemical Characteristics of Clustered Lakes in Southwest Nova Scotia

Cluster number	Number of lakes sampled	Centroid Values						
		pH	Conductance (µS/L)	Colour	SO_4^{2-} (mg/L)	Cl^- (mg/L)	Ca^{2+} (mg/L)	Alkalinity (mg/L $CaCO_3$)
1	15	5.4	26	25	2.4	4.3	0.5	.17
2	13	4.8	31	103	3.3	4.8	0.5	.09
3	6	5.8	46	11	3.5	9.6	1.4	2.5
4	2	6.7	55	5	7.5	10.7	1.0	.8
5	3	5.8	84	6	3.9	18.2	2.6	7.2
6	3	5.3	66	52	5.1	15.8	1.9	4.0
7	1	6.5	72	17	2.8	15.7	2.0	5.0

Table A-5. Chemical Characteristics of Clustered Lakes in Newfoundland

Cluster number	Number of lakes sampled	Centroid Values							
		pH	Conductance (µS/L)	Colour	TOC (mg/L)	SO_4^{2-} (mg/L)	Cl^- (mg/L)	Ca^{2+} (mg/L)	Alkalinity (mg/L $CaCO_3$)
1	7	6.2	24	58	11	2.1	1.7	1.7	.17
2	7	5.8	26	95	17	2.8	1.6	1.6	.09
5	7	6.4	29	34	9	1.9	1.9	1.9	2.5
7	7	6.2	24	15	7	1.6	1.3	1.3	.8

Table A-6. Water Quality Branch Acid Precipitation Lake Monitoring Sites in Nova Scotia

NAQUADAT No.	Name	Latitude	Longitude
01NS01ED0001	Back Lake in middle	44°17'35"	65°16'04"
01NS01ED0002	Big Dam West Lake in middle	44°27'33"	65°17'30"
01NS01ED0003	Big Dam East Lake in middle	44°26'53"	65°16'00"
01NS01ED0004	Mountain Lake in centre of north part	44°19'40"	65°15'51"
01NS01ED0005	Peskowesk Lake NW of tip of Isle de l'Orignal	44°19'00"	65°16'59"
01NS01ED0006	Grafton Lake in centre	44°23'08"	65°10'40"
01NS01ED0007	Kejumkujik Lake 200 m SW of Peale Island	44°22'09"	65°13'14"
01NS01ED0008	High Lake in middle	44°21'20"	65°15'29"
01NS01ED0010	Pebbleloggitch Lake in middle	44°18'06"	65°21'06"
01NS01ED0011	Coblielle Lake in middle	44°19'00"	65°13'59"
01NS01ED0013	Ben Lake in middle	44°20'39"	65°19'59"
01NS01ED0014	Big Red Lake	44°20'58"	65°22'59"
01NS01ED0015	Mud Lake in middle	44°16'49"	65°13'14"
01NS01ED0016	Snake Lake in middle	44°21'24"	65°12'24"
01NS01ED0017	Liberty Lake in middle	44°23'08"	65°25'36"
01NS01ED0019	Frozen Ocean Lake in middle	44°27'07"	65°20'44"
01NS01ED0020	Central Lake	44°25'00"	65°18'33"
01NS01ED0021	Little Red Lake at SE side	44°20'20"	65°23'44"
01NS01ED0022	Poplar Lake in middle	44°21'15"	65°26'20"
01NS01ED0025	Luxion Lake in middle	44°21'42"	65°20'35"
01NS01ED0027	Beaverskin Lake in middle of west part	44°18'28"	65°19'59"
01NS01ED0028	McGinty Lake in middle	44°21'37"	65°09'38"
01NS01ED0029	Peskawa Lake in middle	44°19'04"	65°21'45"
01NS01ED0030	Upper Silver Lake in middle of south basin	44°16'59"	65°14'48"
01NS01ED0043	Mount Tom Lake, Kejumkujik National Park	44°22'05"	65°18'00"
01NS01ED0047	George Lake, Kejumkujik National Park	44°20'26"	65°13'14"
01NS01EA0010	Trefry Lake 300 m NNE of outlet	43°50'07"	66°02'38"
01NS01EA0011	Allen Lake	43°56'47"	66°09'11"
01NS01EA0013	Milton Lake just north of centre	43°51'42"	66°06'47"
01NS01EA0014	Churchill Lake about 300 m SW of inlet	43°59'26"	66°08'21"
01NS01EA0016	Darling Lake 300 m south of inlet from Coggins Lake	43°58'05"	66°07'17"
01NS01EA0002	Lake George, 15 km NE of Yarmouth (water supply)	44°00'00"	66°04'00"
01NS01EA0004	Jesse Lake, Yarmouth Co.	44°01'59"	66°00'29"
01NS01EA0005	Doctor Lake 300 m SW of large island	43°53'13"	66°05'57"
01NS01EA0009	Brenton Lake near centre	43°57'41"	66°04'09"

Table A-6. Continued

NAQUADAT No.	Name	Latitude	Longitude
01NS01DA0002	Tedford Lake, Digby Co.	44°06'00"	66°01'00"
01NS01DA0003	Killam Lake 250 m NW of inlet from Lake George	44°00'02"	66°04'55"
01NS01DA0004	Cedar Lake 100 m SW of large point at north end	44°01'35"	66°06'38"
01NS01ED0048	Loon Lake, Kejimkujik National Park	44°22'15"	65°14'30"
01NS01DA0005	Lower Corning Lake 550 m SE of Corning Brook	44°03'01"	66°04'58"
01NS01DA0006	Pierce Lake 175 m west of NE shore	44°07'09"	66°05'49"
01NS01DA0007	Coggins Lake about 300 m north of southern shore	43°58'41"	66°06'29"
01NS01EA0019	Snarl Lake 440 m NE of NW outlet	44°06'20"	65°58'32"
01NS01EA0020	Bird Lake about 200 m east of NW shore	43°58'23"	65°56'39"

Results from the first two sampling runs are complete and show that lake chemistry is generally similar at both sampling times in both areas.

Once several years of data are produced, they can be analyzed for trends in a number of ways. Analysis of variance techniques, as well as the non-parametric methods, can be used to determine between-year differences within the various clusters or to answer other questions of interest.

A.4 PARAMETER SELECTION

A detailed list of the parameters analyzed in all samples of the WQB-AR monitoring program is given in Table A-8.

A.5 FIELD QUALITY CONTROL

Quality control in the field consists of:

(a) triplicate samples taken at random sites, approximately once every seven samples, to ensure that the data are reproducible;

(b) blanks done every sampling day to ensure that no contamination of metal samples by preservatives occurs;

(c) shipping within 48 hours of all samples to the laboratory to ensure that immediate analysis is done on those parameters requiring it.

An additional field quality control procedure done at each site is a temperature profile to ascertain that stratification has not yet occurred. Table A-3 shows that most of the region's headwater lakes are shallow and do not stratify. The rapid flushing rates of many of the lakes (Kerekes, 1975) also ensure that little stratification occurs.

A.6 DISCUSSION

In trying to determine trends of sulphate and calcium in rivers using time-series analysis, the fall peaks in the concentration of these two ions obscures any long-term trends (Freedman *et al.*, 1985). Another complicating factor is that historical sulphate data from coloured waters were overestimated due to the interference of colour in the analytical method used at the time. This overestimation was greatest in the fall, which caused increased skewness in the data, rendering it more difficult to process using time-series analysis. Both of these problems are now resolved,

Table A-7. Water Quality Branch Acid Precipitation Lake Monitoring Sites in Newfoundland

NAQUADAT No.	Name	Latitude	Longitude
01NF02YH0001	Wigwam Pond	49°16'59"	57°43'59"
01NF02YK0006	Centre of Glover Island	48°47'45"	57°39'37"
01NF02YL0001	East of Adies Pond	49°24'28"	57°13'18"
01NF02YM0001	Near Noble Pond	49°49'05"	55°54'51"
01NF02YM0003	North of Upper Indian Pond	49°32'29"	56°38'16"
01NF02YM0006	Near Middle Arm	49°44'29"	56°10'01"
01NF02YM0007	NW of Burlington	49°50'39"	56°05'44"
01NF02YN0008	Sandy Lake SW of Buchans	48°49'04"	56°56'43"
01NF02YP0007	Gull Lake	48°56'02"	55°21'51"
01NF02YP0009	Tally Pond	48°36'34"	56°29'27"
01NF02YQ0001	Bellman's Pond	49°10'46"	54°39'07"
01NF02YR0005	Near Ocean Pond and T.M. Pond	49°12'05"	54°08'00"
01NF02YS0003	Rattle Pond	48°30'50"	53°49'28"
01NF02YS0005	Shallow Pond #3	48°30'15"	53°49'30"
01NF02YS0009	Ochre Hill Pond	48°30'10"	53°57'50"
01NF02YS0010	Chatman Pond W.	48°29'39"	53°59'03"
01NF02YS0016	Nameless Pond #2	48°33'00"	53°51'00"
01NF02YS0021	Bog Pond	48°29'39"	54°07'59"
01NF02YS0029	Long Waters S.	48°27'29"	54°03'20"
01NF02YS0045	Jay Pond	48°38'12"	53°53'03"
01NF02YS0048	Mosses Cove Pond	48°35'48"	53°45'16"
01NF027B0001	Big Pond	47°50'54"	58°13'18"
01NF027C0002	Near Knowle's Brook	47°48'06"	57°18'43"
01NF027C0003	Stephenson's Pond	47°54'45"	57°29'47"
01NF027D0001	Near Dollard Brook	47°48'39"	56°34'54"
01NF027D0002	Pond W of Wolf Lake	48°04'31"	56°41'33"
01NF027F0003	Pond N of Gisbourne Lake	47°50'03"	54°49'13"
01NF027F0004	Hungry Grove Pond	47°50'42"	55°07'00"
01NF02YH0011	Unnamed pond	49°33'40"	57°43'30"
01NF024H0012	Unnamed pond	49°31'30"	57°42'30"
01NF024H0013	Unnamed pond	49°35'45"	57°44'00"
01NF02YH0014	Unnamed pond	49°26'15"	57°32'00"
01NF02YH0015	Unnamed pond	49°27'30"	57°31'50"
01NF024H0010	Unnamed pond	49°29'50"	57°32'30"

and corrections can be applied to new data to allow the method to give accurate trend estimations.

The Atlantic Region's acid precipitation effects monitoring covers the sensitive areas of Atlantic Canada. The sampling frequencies used in both river and lake networks have been chosen to provide necessary data at a reasonable level of expenditure based on current knowledge and expertise. Both the aerial coverage and the sampling frequency can be modified should improved field, laboratory, or statistical methodologies justify it. In all three aspects, improvements are constantly being investigated for implementation, though not at the expense of some level of continuity in the data set.

All the emphasis in water quality monitoring has been put on water chemistry because work on the use of biological indicators of acidification was

Table A-8. Parameters Measured in the Acid Precipitation Effects Monitoring Network in the Atlantic Region

Field
Water temperature
pH
Instantaneous or mean daily discharge (rivers only)
Specific conductance
Laboratory
Colour (Nessler relative units)
Conductivity ($\mu S.cm^{-1}$)
pH
Turbidity (JTUs)
Alkalinity (Gran and/or Total - depending on pH)
Sulphate (MTB, $mg.l^{-1}$)
Sulphate (Ion chromatograph, $mg.l^{-1}$)
Chloride
Fluoride
Calcium
Magnesium
Potassium
Sodium
Silica (reactive)
Iron (extractable)
Manganese (extractable)
Copper (extractable)
Zinc (extractable)
Cadmium (extractable)
Lead (extractable)
Aluminum (extractable)
Carbon (dissolved organic)
Nitrogen (total)
Nitrate-nitrite
Humic acids (fluorometry)
Total phosphorus

still at the survey stage in the region until recently. The use of biota for monitoring trends in any routine study requires that the biological component be ubiquitous within the network, be easily collected and identified, and be amenable to an acceptable type of interpretation.

One biotic component that answers these needs is the diatoms in the water column. They are found in all lakes, are easily collected and identified, and analyses such as Nygaard and species diversity have been well developed. In the spring of 1984, WQB-AR collected samples at all of its lake-monitoring sites to determine if the diatoms and other phytoplankton populations correlate to the lake groupings that were based on water chemistry. If they do, a useful tool will have to be developed for using biota as long-term monitors of acidification. If not, further research will have been indicated.

A.7 CONCLUSIONS

The data collected in this monitoring program are being used in a number of other studies dealing with LRTAP, e.g., in the development of geochemical models (Thompson, 1982) and in the assessment of analytical methodology, especially for sulphate and aluminum.

The analysis of trends in water quality is a difficult task. Not all parameters behave the same way, so that several statistical methods might have to be used to answer different questions. This problem, plus the usual logistic and resource limitations, suggests that a monitoring program should be as broadly based as possible so that the data being made available in the future will be suitable for different types of manipulation. The needs of data users in the future might change as more becomes known of the dynamics of basins, of statistical techniques, and even of control strategies. Present monitoring programs have to try to anticipate some of these needs. The WQB-AR program is attempting to do this, while at the same time providing numbers that can be used with present-day knowledge and techniques.

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Appendix B
LRTAP Aquatic Effects Monitoring—Quebec Region

APPENDIX B

LRTAP AQUATIC EFFECTS MONITORING–QUEBEC REGION

B.1 INTRODUCTION

Data available on the source and quality of precipitation reaching Quebec show the importance of the St. Lawrence River corridor in LRTAP (Désautels, 1981; Harvey *et al.*, 1981; Barrie and Sirois, 1982; Barrie *et al.*, 1982). The geological formations of the southern part of the province are also centred in this corridor. Aside from the carbonate-rich rocks in the Gatineau basin and the immediate area of Lac Mistassini, all of the Canadian Shield north of the St. Lawrence River is considered to be very sensitive to acidification from airborne loads (Altshuller and McBean, 1979; Harvey *et al.*, 1981; Shilts, 1981).

Although the Appalachian south shore of the St. Lawrence River has been somewhat overlooked, the area as a whole is, in spite of thick litter and the high carbonate content of certain layers of rock, of average to high sensitivity (Harvey *et al.*, 1981; Shilts, 1981).

The impact of acidification has been the subject of various studies intended mainly to survey areas in the southern part of the province as a whole (Grimard, 1981; Legendre *et al.*, 1980; Bobée *et al.*, 1982), in the Shield (Langlois *et al.*, 1983), and in even smaller areas (Richard, 1982; Magnan, 1982; Dupont, 1983) with different levels of sensitivity and acidity.

These studies made it possible to define a target area representative of variations in acid loading and mineralization in the Shield located north of the St. Lawrence, between the Ottawa and Saguenay rivers, south of the 49th parallel. During the winter of 1982, the IWD-QR sampled 185 lakes in order to determine the quality of the aquatic environment of the Laurentian Highlands and identify, if possible, certain factors that control acidification.

This data bank was created at the same time that it appeared there was a need to develop a national network for detecting long-term trends (Section 1.0). Consequently, these data were used to design the Quebec portion of the network.

B.2 OBJECTIVES

The network's two objectives are to detect spatial and temporal trends in changes in the acidification of surface waters in Quebec for various acid loading and sensitivity conditions. These objectives come under one of the objectives of IWD-Quebec Region, which is to determine the capacity of the Quebec ecosystem to resist the effects of the long-range transport of air pollutants.

In case of conflict in attaining these objectives (e.g., the impossibility of attaining temporal and spatial aspects simultaneously because of a lack of resources), it is recommended that priority be given to detecting trends (i.e., temporal changes) at a limited number of sites. The implementation of the Quebec component of the network is based on this recommendation.

B.3 HYPOTHESES

The network design is based on the following hypotheses:

(a) The regional differences in the quality of water are unchanging and representative of the area covered.

(b) Similarly, the lakes selected are representative of their population (in the statistical sense), and from the samples, it is possible to measure effectively the characteristics that are most relevant to changes in acidification.

(c) The meteorological regime is more or less constant over the long term so that a change in emissions affects the quality of the environment.

(d) No human activities or major disturbances (logging and the like) will be carried out in the selected basins during operation of the network.

B.4 SITE SELECTION CRITERIA

B.4.1 Macrolocation

The neutralizing ability of the basins depends to a large extent on their geological and geomorphological characteristics, which are highly regional in nature. The best estimate, i.e., the one that has the lowest variance, of the regional value is given by the arithmetic mean. The degree of homogeneity of this variable for the region under consideration may be quantified by the variance (standard deviation) of this variable.

The procedure for setting up the network was as follows. Regions that are homogeneous from the viewpoint of quality were established. [A factor showing airborne acid loading (sulphates in surface water) and a variable determining the level of acidity in the environment (pH) were combined with the most relevant mineralization variables (alkalinity and $Ca^{2+} + Mg^{2+}$).] Processing of the data for the Inventaire project by multivariate analysis divided the area into five regions as illustrated in Figure B-1. The characteristics of these regions appear in Table B-1.

At least two sampling sites that were representative of the average regional conditions were chosen in each of these regions. Samples were taken more frequently at these stations in order to obtain a long series of data quickly. These data will be tested under the zero hypothesis (Ho) that there are no trends in water quality. The statistical model, which uses time-series analysis, is the one developed by Lettenmaier (1978, 1979).

Additional stations for less frequent sampling were selected in order to verify the regional representativity of the "temporal" sites and changes in the spatial pattern. This method of selecting sampling regions and their sites served as the basis for designing the network for detecting spatial and temporal trends for lakes as well as rivers. The method uses a "fixed" geographic division (geological and geomorphological), which implicitly accepts that the grouping is stable and representative and that spatial variability thus detected is representative.

This procedure, detailed in Bobée *et al.* (1983), is an alternative to the American sampling plan proposed by Powers *et al.* (1983), which recommends groups of at least six lakes to represent each region, and calls for considerable resources. The procedure used here can be transposed to any other region.

Table B-1. Regional Averages of Discriminating Variables and Confidence Intervals to 90% on these Averages

Region	No. lakes sampled	Alkalinity (μeq/L)	Ca + Mg (μeq/L)	pH	SO_4 (μeq/L)
1	20	22.6 ± 3.4	90.5 ± 3.0	5.40 ± 0.08	77.9 ± 3.7
2	44	37.2 ± 3.7	127.3 ± 3.8	5.59 ± 0.06	105.5 ± 3.1
3	41	166.0 ± 13.4	221.6 ± 10.1	6.23 ± 0.05	83.2 ± 3.7
4	29	170.6 ± 19.3	283.3 ± 19.9	6.42 ± 0.05	134.6 ± 4.5
5	17	493.9 ± 66.4	627.8 ± 67.2	6.84 ± 0.11	183.0 ± 13.1

Note: For various reasons (litter, vegetation, etc.), the following lakes do not belong or seem to belong to the regional populations of headwater lakes and have been excluded: lakes 34 and 47 (region 3), lake 144 (region 4), and lakes 17, 26, 27, and 29 (region 5).

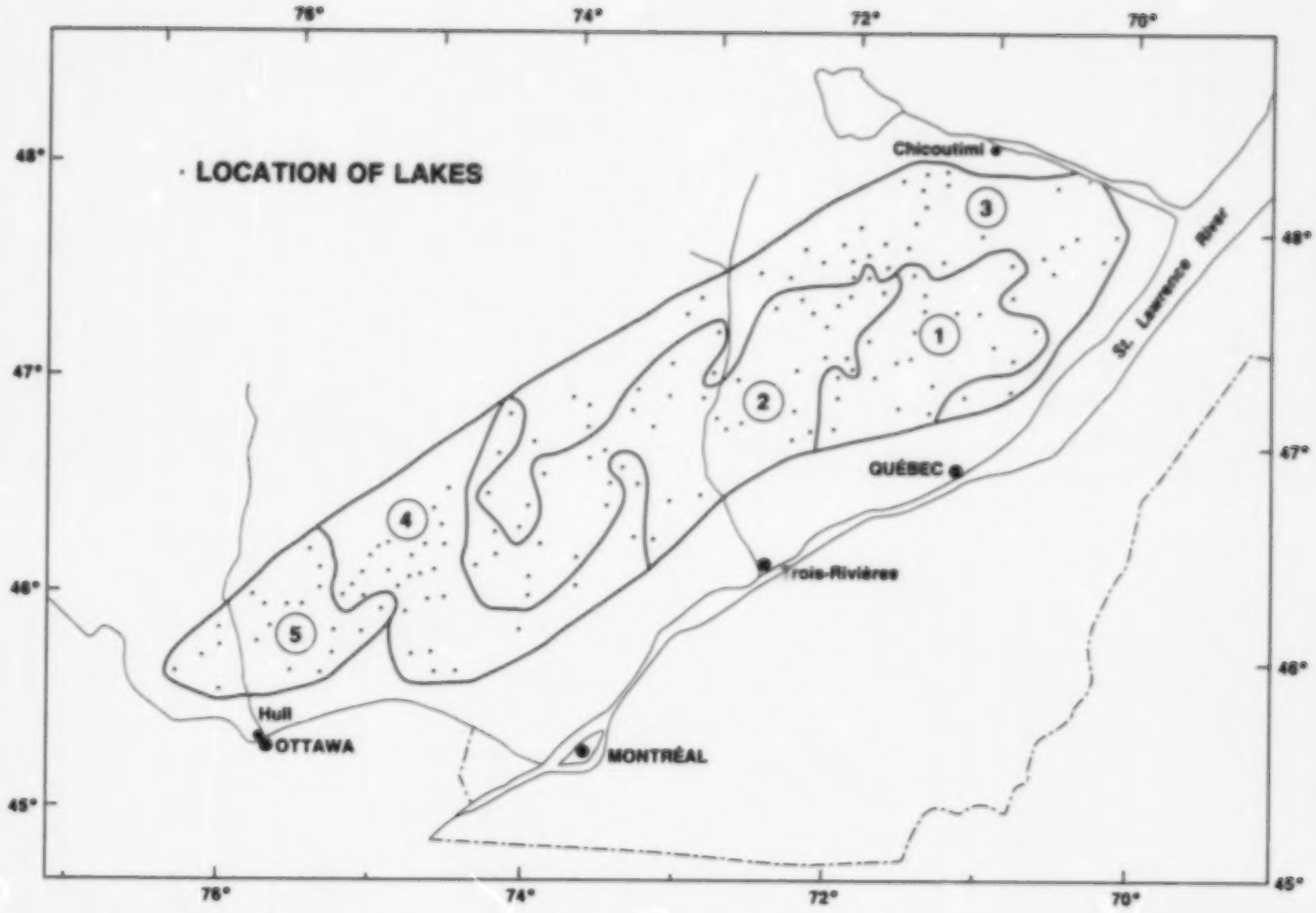

Figure B-1. Division of the area into regions with homogeneous physico-chemical concentration (mg/L).

B.4.2 Microlocation - Choice of Sites

B.4.2.1 *Lakes*

B.4.2.1.1 Physico-chemical Characteristics

The "temporal" stations were chosen such that their median values were as close as possible to the median values for the region of the following values: pH, alkalinity, and $Ca^{2+} + Mg^{2+}$ and SO_4^{2-} concentrations. In addition, to avoid significant interference from organic matter, the water colour at any site must have been less than 50 Pt units. Aerial photographs were used to check the absence of peat and the characteristics of the litter and the lithology. In case of doubt, these factors were verified during the sampling trips.

The "spatial" stations were selected in a totally random fashion (drawn from an urn), then checked for colour, vegetation, and litter in the same way as the previous stations.

B.4.2.1.2 Physiographic Characteristics

In general, the sites chosen must cover, in a representative fashion, the morphometric variables considered in the multivariate analysis, particularly where the range is very extensive and makes it impossible to separate the regions (for example, elevation in regions 1 and 4). For variables with reduced variance in each group and a different range of variation in each zone, this recommendation is less important. The "temporal" stations should be representative of the median values of the following characteristics: elevation, ratio of areas (lake and basin), and depth.

The hydrological order of the lake is extremely important because of the numerous interactions between the acid loads and the various components of a watershed that affect the quality of the surface water. The sites where the acid loads are most directly perceivable and most easily isolated are headwater lakes. Located at the heads of basins, these are simple hydrological systems which, because of their small size, present greater geological, geomorphological, pedological, and phytosociological homogeneity than larger basins.

The lakes chosen as sampling sites for the network are free of major disturbances resulting from human activities such as controlling dams, forest cutting, industries, mines, roads, cottages, and high voltage lines, and the basins are free from significant organic deposits.

B.4.2.2 *Rivers*

Except for the hydrological order, the criteria for rivers are the same as for lakes, where applicable. To these, the following were added: the size of the basin should be less than 100 km^2, if possible; the soil should be the thinnest possible; and the river should be gauged or gaugeable.

B.5 FREQUENCY

B.5.1 Lakes

Detecting a trend at least equal to the standard deviation of the time series is recommended. A stricter requirement, one half of the standard deviation, for example, risks being unrealistic (Lettenmaier, 1977). Detecting trends is possible only if comparable data covering a sufficiently long period of time are available (Sherwani and Moreau, 1975).

Studies of rivers showed that in detecting trends, more frequent sampling is much more important in network design (reduces the variance of a statistical parameter, in this case, the annual average) than the spatial distribution of stations, regardless of the water quality variable considered and the size of the trend (Lettenmaier and Burges, 1977). Although these results were obtained from a network operating in particular conditions (four years of measurements of very highly mineralized water), the auto-correlation structures for populations of water quality variables were approximately the same as for Lac Laflamme. The temporal variability of this gauged basin is considered to be representative of lakes in the Laurentian Highlands.

Lettenmaier (1977) provides tables that give the total size of the sample to be taken over five or ten years in order to detect a trend, expressed as a proportion of the standard deviation of the residuals of the series for different values of the test power and different daily self-correlation coefficients (ρ_1). Using the data from Lac Laflamme, it is possible to determine the size of the sample to be taken and thus the frequency of sampling.

If $\rho_1 = 0.85$ and a period of five to ten years is considered, it is only by doing a minimum of six measurements a year at constant intervals (size of sample to be 30 to 60 on a five-year period of measurement) that one has any hope of finding a trend after six years and before ten years of measurement. This sample size should, however, be reassessed on the basis of the first years of data provided by the network.

This relatively high frequency of sampling is recommended for the "temporal" stations. "Spatial" stations require a minimum of two measurements a year. (This way, there will be at least ten values after five years of operation.) Although the ideal would be to take the samples under isothermal conditions in the spring and fall, logistic and financial constraints make this almost impossible (e.g., difficulty of determining the moment of measuring a remote site, impossibility of returning there, and nonrepresentative nature of spatial averages). To optimize the acquisition of data it is recommended that "spatial" stations be sampled at the same time as "temporal" stations.

B.5.2 Rivers

Compilation of quality data on the Eaux Volées stream (Service de qualité des Eaux, 1979) shows that the weekly self-correlation coefficients are of the same magnitude as for Lac Laflamme. On the other hand, Bobée and Cluis (1979) showed that the water quality variables for Quebec rivers could present considerable data redundancies, even with monthly sampling. This is why the same sampling frequency of six times a year at two-month intervals is recommended for rivers, although initially it would be desirable to double this for better rationalization of the network.

B.6 WATER QUALITY VARIABLES

The list of water quality variables to be measured consists of major ions, silicate (measured for a better understanding of the alteration of silicates and aluminosilicates in the neutralization process), and Al, Mn, and Fe (measured because their solubility seems related to the acidity of surface waters) (Harvey *et al.*, 1981).

The sampling is carried out by taking an integrated sample from the surface to a depth of 5 m (or 2 m from the bottom if the depth is less than 7 m). This aspect is still being discussed, and the sampling method might change for the sake of uniformity throughout the network. The detection of long-term trends requires measurements that are strictly comparable in time. It is very difficult to detect trends if the number, location, and sampling methods vary with the stratification conditions of the water.

The analytical methods are the ones used by the National Water Quality Laboratory in Burlington (Environment Canada, 1981).

B.7 IMPLEMENTATION OF THE NETWORK

Regional homogeneity, sampling frequency considerations related to detecting trends, spatial coverage, and the resources available affected the preliminary choice of sites for the network.

During the first year, 10 "temporal" stations and 20 "spatial" stations were operated on lakes, and none on rivers. In total, 100 samples were collected.

The complete surveys were carried out in the spring and fall during isothermal conditions.

Taking into account the occurrence of important limnological events (spring and fall isotherms, appearance and disappearance of ice), the sampling schedule was set as follows:

- late May - early June (complete survey - 35 lakes)
- late July - early August (10 lakes)
- late September - early October (10 lakes)
- late November - early December (complete survey - 35 lakes)
- late January - early February (10 lakes)
- late March - early April (10 lakes)

Given the structure of the network, the method of travel (helicopter), the relative stability of the parameters, the availability of laboratories, and the means of transportation, the tolerance over the two-month period is approximately plus or minus three days.

The locations of the stations appear in Table B-2.

The network has been operating since May 1983 and still requires some adjustments in the areas of sampling protocol, sample preservation, and analysis.

Table B-2. Environment Canada, Quebec Region, Lake Monitoring Sites

NAQUADAT No.	Name	Latitude	Longitude
01QU02LD0005	Blais	45°56'00"	75°10'00"
01QU02LF0003	Graham	45°48'00"	75°23'00"
01QU02LF0004	Sheridan	45°44'00"	75°37'30"
01QU02LH0187	Duck	45°50'30"	75°51'30"
01QU02LH0185	Bohême	45°52'30"	76°07'00"
01QU02LH0186	Clair	45°36'00"	76°04'00"
01QU02LF0002	David	45°18'30"	75°35'00"
01QU02LD0004	Papillons	46°06'30"	75°20'00"
01QU02LD0010	Kidney	46°12'30"	75°14'00"
01QU02LD0008	Griffin	46°03'30"	75°01'00"
01QU02LD0009	Chevreuil	46°03'00"	74°56'00"
01QU02LD0011	SN 19222	46°08'30"	74°58'00"
01QU02LC0016	Général-White	46°22'00"	74°41'00"
01QU02LC0015	Truite Rouge	46°09'00"	74°05'00"
01QU020B0002	Laurent	46°28'30"	74°12'00"
01QU02NF0001	Adanys	46°48'20"	74°19'30"
01QU02NF0005	Nolette	47°05'00"	73°47'30"
01QU02NF0002	36724	46°45'30"	74°02'40"
01QU020C0002	Jones	46°45'00"	73°23'00"
01QU020C0003	Thibert	46°39'00"	73°10'00"
01QU02NF0003	Eclair	46°51'20"	73°00'10"
01QU02PB0002	Najoua	47°02'30"	72°05'00"
01QU02NE0001	Fauvette	47°20'20"	73°14'00"
01QU02NE0002	92844	47°38'30"	73°02'30"
01QU02NE0003	Chômeur	47°50'00"	72°13'00"
01QU02PA0002	Congré	47°42'00"	72°01'40"
01QU02RG0001	Daniel	47°47'20"	71°48'20"
01QU02RG0002	Lemaine	47°43'10"	71°46'10"
01QU02PF0001	35759	47°49'30"	70°35'40"
01QU02RH0001	Thomas	47°53'00"	70°14'30"
01QU02PD0002	McLeod	47°28'00"	70°58'40"
01QU02PC0001	Bonneville	47°16'40"	71°24'20"
01QU02PB0004	Veilleux	47°23'40"	71°34'30"
01QU02PB0005	Josselin	47°22'00"	74°40'00"
01QU02PB0003	Lagou	47°18'15"	71°49'20"
01QU02PD0001	Laflamme	47°19'25"	71°07'35"

Blanks and triplicates of samples were not taken for the first year since the emphasis was on knowledge of the area's characteristics instead of accuracy. They also require a substantial increase in resources.

It was also difficult to comply with all the constraints regarding the choice of sites, especially the absence of human activities. Forest roads provide access to many small headwater lakes, and activities related to hunting and fishing are

present everywhere (camps, cottages, rowboats, fires) except in parks and reserves.

The first two years of operation were reserved for adjustments to the network design, after which the measurements were stabilized. At the moment, the hypotheses on which the network design was based have not all been verified (regional representativity and the like) since there are not sufficient data points available yet. In addition to the physico-chemical data, descriptions of the geological, physiographic, and phytosociological characteristics of the basins are being collected in collaboration with Lands Branch.

The current network for testing the quality of surface waters in relation to the acid rain problem should make it possible to monitor changes in the acidification of lakes in a limited area in southern Quebec. The network, however, does not adequately cover all areas subject to acidification, nor all sensitive regions in the southern half of Quebec.

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Appendix C

Long-Term Monitoring of Surface Waters — Recommended Methods for the Collection and Analysis of Water Samples

APPENDIX C

LONG-TERM MONITORING OF SURFACE WATERS–RECOMMENDED METHODS FOR THE COLLECTION AND ANALYSIS OF WATER SAMPLES

C.1 INTRODUCTION

The objective of this appendix is to review existing water quality sampling and analytical procedures and to recommend methodologies for a LRTAP aquatic effects monitoring network. For a discussion of the monitoring objectives, siting criteria, and parameter selection, see Sections 1.0, 2.0, and 3.0. Information will only be repeated here where it is relevant to the methodologies covered by this appendix.

Specific topics addressed include the following:

- Sample collection methods
- Sample handling procedures
- Sample history
- Analytical methodology

This appendix is restricted to a discussion of water chemistry monitoring. The LRTAP aquatic effects monitoring network, however, is based on a multi-media sampling approach. Protocols for the sampling of media other than water will be developed separately.

These protocols are drawn from existing work by the Ontario Ministry of Environment (1979), McQuaker *et al.* (1983), and Scheider *et al.* (1983).

One of the key requirements for a successful long-term monitoring program is consistency. Once a monitoring program has been implemented, the fewer changes made to the techniques used, the more comparable the data will be over time. If it is necessary to make changes due to improved technology, methodology, or any other reason, sufficient quality control samples must be taken to ensure the equivalency of the methods.

C.2 SAMPLE COLLECTION METHODS

C.2.1 General

The sampling procedures should allow for the isolation of a representative sample and should minimize the potential for chemical alteration of the sample including the effects from biological activity. All containers used for either sample collection or shipping must be free of detectable levels of the parameter of interest. Volumes sampled should be sufficient to fill the sample container, minimizing the residual air space.

C.2.2 Lakes

The principal monitoring site is located at the deepest point in the lake. For larger lakes where there is more than one sampling site per lake, the sites should be located at the deepest point of each distinct basin (or segment) of the lake, and sampling at each site must accommodate non-uniform vertical mixing of dissolved (and suspended) chemical constituents. Satellite sites may be eliminated if they are shown not to be chemically distinct from the principal site.

Recommended sampling procedures are listed below. The alternatives given take into account the importance of thermal stratigraphy in lakes, and a temperature profile must be taken when it is required to determine the location of mixed layer boundaries.

Three methods are recommended and will be described below. These are a surface grab sample, a non-volume-weighted composite sample, and a discrete sample taken at the mid-point of each mixed layer. Two other methods of sample collection, the single volume-weighted composite sample and a separate volume-weighted composite sample from each mixed layer are used at research study sites where accurate mass balance calculations are required. These methods, however,

are not convenient for an operational monitoring network where a large number of lakes must be sampled by helicopter in a short period of time.

C.2.2.1 *Surface Grab Sample*

A surface grab sample at 1 m depth, may be taken providing a temperature profile indicates that no vertical temperature gradient exists and the lake is well mixed.

C.2.2.2 *Non-volume-weighted Composite Sample*

A non-volume-weighted composite sample can be taken through a depth equivalent to the thermocline depth in midsummer or 1 m above the lake bottom if the lake does not stratify. The following method should be used.

(a) Identify the required sampling depth.

(b) Select a sampling tube with an appropriate internal diameter (ID). The total volume sampled should be approximately equal to and not greater than the capacity of the sample container (e.g., 4 L). The sampling tube should be flexible, clear plastic tubing with a suitable weight at one end.

(c) Lower the weighted end of the sampling tube to the desired depth; pinch the tube just at the surface and raise the tube from the bottom; then transfer the contents to a sample container. Rinse the tube and sample container at least twice with surface water before use.

C.2.2.3 *Discrete Sample at Mid-point of Each Mixed Layer*

To take a discrete sample, one must

(a) identify the required sampling depth(s),

(b) use a suitable sampler to remove the sample and transfer to a sample container. Rinse the sample container at least twice with surface water before use.

C.2.3 Rivers

Surface grab sampling is acceptable in rivers. Rinse the sample container at least twice with the water to be sampled. To collect the sample, hold the sample container just under the surface of the water until completely full.

C.3 SAMPLE HANDLING PROCEDURES

C.3.1 Sample Containers

The following container materials are recommended. Containers to be used for pH, alkalinity, major ions, and trace metals should be composed of high density linear polyethylene with polypropylene caps. For total phosphorus and mercury samples, glass Sovirel bottles should be used. The bottle size required will depend on the volume of sample required by the laboratory.

C.3.2 Sample Filtration

To determine the concentration of dissolved inorganic constitutents (e.g., metals and anions), it is necessary to filter the sample through a 0.45-µm membrane filter as soon as possible after collection.

C.3.3 Sample Transportation

The time between sampling and arrival of the sample at the laboratory should be minimized. Prior to transit, the sample must be stored at 4°C. Time in transit should not exceed 72 hours and coolers must be used.

C.4 SAMPLE HISTORY

Sample history provides information for a particular sampling event and is used to provide relevant information for the data base. It is recommended that sample history be documented in the form of a report that includes the following;

(a) site identification

(b) operator identification

(c) date of sampling

(d) sampling procedure including sampling depth

(e) volumetric flow rate (rivers only)

(f) temperature profile (lakes only)

(g) time in transit

The following information should be entered into the data base: site identification, date of sampling, site description, sampling procedure, volumetric flow rate (rivers only), temperature profile (lakes only), and analytical results. If time in transit exceeds 72 hours, for an unpreserved sample, all analytical results entered into the data base for that particular sample should be flagged.

C.5 ANALYTICAL METHODOLOGY

For field measurement procedures, refer to "Sampling for Water Quality" (Water Quality Branch, 1983).

Detailed descriptions of laboratory analytical methodology are generally outside the scope of this appendix. Methodologies have been recommended, however, for two parameters. These are total alkalinity, which for soft waters should be measured using Gran plot calculations (a negative alkalinity value should be reported), and sulphate, which should be measured using the ion chromatograph.

All laboratories analyzing samples from the LRTAP aquatic effects monitoring network must use analytical methods approved by the Research and Monitoring Coordinating Committee (RMCC) Quality Assurance Subgroup and must take an active part in the quality assurance program.

Further information on the analytical methodology can be obtained from Campbell (1983) and the Water Quality Branch's *Analytical Methods Manual Update* (1981).

C.6 QUALITY ASSURANCE/QUALITY CONTROL (QA/QC)

QA/QC procedures are outside the scope of this appendix, but are to be defined in cooperation with the RMCC Quality Assurance Subgroup (see Aspila *et al.*, 1983, and Water Quality Branch, 1986).

C.7 REPORTING PROCEDURES

The procedures used to archive the data and the reporting procedures are outside the scope of this appendix. It has been suggested (April 10, 1984, meeting of Monitor Task Group) that NAQUADAT be used to archive the data. Reports summarizing the results should be prepared and reviewed by the agencies taking part in the program (see Section 8.0).

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